

MODERN ELECTROPLATING

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General Principles

WILLIAM BLUM * AND WALTER R. MEYER †

The purpose of this general chapter is to summarize those principles and methods that may find application in the plating of various metals. Since 1940 there has been a considerable expansion of electroplating, both in methods and in applications. Much of this progress is related directly or indirectly to military problems. Since 1945 the increased demand for consumer goods has stimulated the development of more efficient and more economical procedures in plating and in other fields. This demand, and a scarcity of qualified research workers, may have retarded progress on fundamental problems in electrodeposition, upon which more research is greatly needed. Fortunately, during this period, the American Electroplaters' Society and many industrial firms have expanded their researches, the results of which will not be fully realized for at least a few years.

It will be observed that in the following pages many more problems are propounded than are solved. The need for basic studies in electrodeposition is now more fully appreciated than in the past. Only through such investigations will plating cease to be largely "rule-of-thumb."

COMPOSITION AND CONSTITUTION OF PLATING SOLUTIONS

TYPES OF SOLUTIONS

The division of plating baths into three types, (*a*) acid, (*b*) neutral, (*c*) alkaline, is helpful, even though they are not sharply defined. In terms of *pH* they may be roughly classified as having *pH* values: (*a*)

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lower than 2; (b) between 2 and 8; and (c) higher than 8. The most common examples are: (a) acid copper and chromium baths, (b) nickel baths, and (c) cyanide baths of various metals.

Since 1940 marked progress has been made in the commercial development of new baths of all types. Fluoborates, long used for deposition of lead and tin, are now employed in acid copper and nickel plating baths. Slightly alkaline pyrophosphate baths are used for zinc, copper, and nickel. Acid sulfamate baths of tin, lead, and other metals have been developed, and various alkylsulfonate plating baths are being investigated. The result is a great increase in the kinds of plating baths that may warrant commercial trial and application. Whether any new bath possesses significant advantages, such as the use of higher current densities or the production of deposits with more desirable physical properties, must be determined by experiment. Even when a difference like an increase in the limiting current density by the use of a fluoborate solution is found, it is still not possible to correlate these results with such measurable properties of the solution as conductivity, metal ion concentration, the pH at which hydrolysis occurs in the cathode film, polarization, viscosity, and surface tension. Until such correlations can be made, the choice of a bath for a specific purpose must be largely empirical.

There have been few marked developments in the electrodeposition of new or unusual metals. Success in the electrowinning of manganese indicates that manganese plating is entirely feasible if a demand for it is justified. Present efforts are directed to the production of the more ductile γ -manganese, instead of the very hard, brittle, α -form normally obtained by electrodeposition. This has been accomplished,^{1,*} but the γ -deposits rapidly revert to the α -form.

Special interest attaches to the possible electrodeposition of "border-line" elements like molybdenum and tungsten (wolfram), thick coatings of which have not thus far been deposited in pure form from aqueous solutions. Recently it was reported² that very thin deposits of molybdenum can be deposited from aqueous solutions of various salts. Alloys of tungsten with iron, cobalt, or nickel have been deposited.³⁻⁶ Efforts are now being made to deposit tungsten, molybdenum, and other metals such as aluminum, titanium, tantalum, and zirconium from non-aqueous baths containing fused salts or organic solvents. If this can be accomplished, and if deposits with good physical properties can be obtained, entirely new methods and applications of electroplating may be developed.

* Superior numbers indicate references, which appear at the end of each chapter.

ACID BATHS

Metal Salt Plus Acid. The most commonly used acid baths contain chloride or sulfate, or mixtures of these salts. Nitrates are seldom used in plating baths because they may be cathodically reduced to ammonia. (It is possible to use nitrates in silver cyanide baths because in this solution the silver ion is more readily reduced than the nitrate ion.) The choice between sulfate and chloride is determined partly by the respective solubilities of these two salts of the metal involved. When, as with nickel and zinc, both salts are quite soluble, the chloride has, for equivalent concentrations, a higher conductivity. In baths of the iron group metals, the chlorides usually show less anode and cathode polarization than the sulfates. However, these differences obviously do not account for the differences in physical properties of nickel, for example, deposited from the two types of bath. While it is entirely possible that complex ions of some kind may exist in small concentrations in solutions of simple salts, with or without the presence of other salts, it is unlikely that they can account for these differences in behavior. These facts illustrate the present empirical basis for most plating processes.

Other acids present as such or in salts in plating baths, e.g., fluoroboric, fluosilicic, sulfamic, and alkylsulfonic, are all relatively strong, and their salts are highly ionized. Although complex ions may be present in small concentrations, they are not likely to account for differences in behavior of these baths. There is at present no sound basis for predicting the specific effects of the anions in plating baths.

Metal Chiefly in the Acid Radical. The principal bath of this type is the chromic acid bath, in which most of the chromium is present in the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, although all baths in use also contain trivalent chromium, which may exist partly as chromic sulfate and partly as chromic dichromate, each of which ionizes to form trivalent chromium ions. These in turn may be present as either the green or the violet modification, the proportions of which may change with the temperature or other conditions. It is not surprising that no completely adequate or very helpful theory of the mechanism of chromium plating has been developed. Kasper⁷ concluded that metal deposition takes place by direct reduction of chromic acid, and not by step-wise reduction through trivalent or divalent chromium. Direct deposition from hexavalent chromium is supported by studies with tracer chromium 51.⁸ Kasper's theory and most of the others assume the existence close to the cathode of a semi-permeable membrane, consisting, for example, of a basic chromium chromate, for the formation

and functioning of which the presence of sulfate or similar anions is essential.

Extensive studies⁹ have shown that the properties of chromium deposits are closely related to their content of oxygen, probably present as Cr₂O₃ or other basic compounds. On the other hand, Snavely and associates,¹⁰ on the basis of x-ray studies, have postulated the formation of chromium hydrides, which determine the crystal form (cubic or hexagonal) and some of the properties of the deposit.

These divergent views have been mentioned here chiefly to emphasize the large amount of research still required to explain the mechanism of a chemically simple solution like the chromic acid bath.

"NEUTRAL" BATHS

Most of the commercial nickel baths fall in this class; that is, they have a pH between 2 and 8. Acid zinc baths are usually between pH 3 and 5, except those used with insoluble anodes (e.g., in the Tainton process), in which the free acid concentration may be greater than 1 N. Chlorides or sulfates, or both, together with boric acid or acetic acid, may be used in nickel baths. These and other salts may be added to increase the conductivity, decrease the metal ion concentration, or increase the anode corrosion. There is not much evidence of complex ion formation with these simple salts, although ammonium salts certainly form complex ions with nickel, especially in the cathode film, where the pH is higher than in the body of the solution.

Just as with chromium, the structure and properties of nickel deposits are closely related to their contents of basic material, such as oxide or basic chloride, or of organic materials derived from the brighteners used. The microscopical examination of such deposits has not thrown much light on the composition or structure or even the location of these inclusions. Other methods, such as electron diffraction, x-ray diffraction, electron microscopy, or tracer techniques, may prove more fruitful in the study of this difficult problem. The important present conclusion is that apparently pure electrodeposits of most metals contain finite and significant amounts of foreign materials. Numerous observations indicate that silver deposited under the most favorable conditions in a silver coulometer may contain detectable amounts of foreign substances.

"ALKALINE" BATHS

The most important alkaline plating baths are the cyanide solutions of gold, silver, copper, zinc, brass, and cadmium. Knowledge of the constitution of cyanide baths is far from satisfactory. Even when the

principal double cyanides that exist in the solid state have been identified, there is no assurance that the same compounds or the corresponding ions exist in the plating baths. Thompson¹¹ has summarized the available information on the coordination compounds believed to exist in cyanide solutions of various metals. Attempts to define the bath constitution by titration of the "free cyanide" content are likely to yield misleading results, because any existing equilibria are disturbed during the titration. Measurements of the potentials of corresponding metal electrodes yield values of the "metal ion activity," such as $10^{-15} N$, which have practically no physical meaning though they may be correlated with the dissociation or instability constants of one or more of the complexes.

The problem is still further complicated by the addition or formation of other compounds such as hydroxide, carbonate, tartrate, cyanate, formate, and ammonia, as well as by the addition agents and wetting agents. In such a solution the determination or computation of free cyanide is usually empirical and is useful chiefly for control purposes, and not as evidence of the constitution of the complexes.

Other alkaline baths include the pyrophosphates, of copper or zinc, for example, and the alkaline stannate bath commonly used for tin plating. Little is known of the constitution of these baths, much less of the mechanism of deposition. In the cyanide and stannate baths the metal to be deposited is principally present in the anions. No present theory adequately explains the process of depositing a metal such as silver from potassium argentocyanide or argentocyanide anions.

RELATIONS OF *pH* TO METAL DEPOSITION

The preceding conventional classification of plating baths emphasizes the importance of *pH* measurements in the control of plating operations. At present almost all large plating processes involve and benefit from control of the *pH* within certain limits. These limits have been fixed almost entirely by trial and error and not by sound prediction.

It is not difficult to explain the principal role of *pH* in simple salt baths such as those involving chlorides or sulfates (as in nickel baths for example). In these baths there are nickel ions and hydrogen ions which compete for deposition at the cathode. The ratio of nickel to hydrogen discharged is a measure of the cathode efficiency (unless other reducible substances like a ferric salt, hydrogen peroxide, or an addition agent are present).

Among the factors that may affect or determine the cathode efficiency of an acid or neutral plating bath are: (1) the values and the ratio of the concentrations (or activities) of the metal ions and the hydrogen ions; (2) the relative positions of the standard potentials of the metal and hydrogen in the electrochemical series; (3) the relative polarizations (or overvoltages) of the metal and hydrogen on a given cathode surface under the prevailing conditions; and (4) the *pH* at which the metal salt hydrolyzes to form basic compounds. All these factors, and especially the last, may likewise affect the limiting current density for that metal and bath.

Because the values of the above properties are known, or can be measured with fair accuracy for simple salt baths, it is possible to make sound predictions of the major effects of *pH* changes in such baths. The effect of *pH* on the cathode efficiency in an acid copper bath will be much less than in a nickel bath because copper is more noble than hydrogen and nickel is less noble. Similarly, the deposition of zinc with a high cathode efficiency from a strongly acid zinc bath, as in zinc electrowinning, can be explained (and might have been predicted) from the high overvoltage of hydrogen on zinc.

It is not easy to predict or explain the minor effects of *pH*, for example the effects upon the physical properties of the deposited nickel. Recent studies¹² have shown that the grain size, hardness, and oxide content of nickel deposits from a given bath may reach minimum values at a certain *pH* and increase with a *pH* change in either direction. It is reasonable to expect that, at a given current density, a decrease in *pH* (i.e., an increase in hydrogen ion concentration) will reduce the tendency for the formation of basic material in the cathode film and its inclusion in the deposits. The observed reversal of this effect probably involves the compensation of two opposing tendencies, for example, crystal size and inclusions. Purely for illustration, small changes in *pH* may influence the formation, charge, and migration direction of any material present in a colloidal state in the cathode film. Observations on the effects of foreign cations, such as of sodium, potassium, and magnesium, on the properties of nickel deposits suggest that they also may influence the behavior of colloids in the cathode film.

There is no simple relation between the *pH* and the tendency of a given bath to form pitted deposits. A lower *pH* and resultant lower cathode efficiency do not usually increase the pitting, even though more hydrogen is then evolved. As is well known, surface tension and the presence of impurities are more important factors in pitting. Their effects may, however, be influenced by the *pH*.

The effects of *pH* are still less predictable when there are present addition agents or brighteners for each of which the optimum *pH* must be defined empirically.

In alkaline baths, such as those containing cyanide, *pH* control is useful, but even more empirical than in acid or neutral baths, partly because less is known about the dissociation or hydrolysis of the complex cyanides (especially in the presence of carbonates and hydroxides) than of simple salts. The extent of hydrolysis of the alkali cyanides is so great that, with sufficient free cyanide, a given *pH* (up to 10) may be reached with sodium cyanide as well as with sodium hydroxide, and the *pH* measurement gives no clue to which is present or is needed. If, as in simple baths, the limiting current density is defined by the precipitation of an excess of basic material, the content of free cyanide and of ammonia (e.g., in brass baths) is probably more determinative than the hydroxyl ion concentration defined by the *pH*.

At present the measurement and control of *pH* in plating operations must be considered a useful, important tool, similar to the control of temperature and current density. The preferred limits of *pH* and the precision required in its control for a given bath and operating conditions must be defined by experiment and experience.

• ADDITION AGENTS

The very great increase in the use of "bright plating" baths, notably of nickel, but also of copper, zinc, and cadmium, has made the use of addition agents the rule rather than the exception. (In this discussion the term addition agent will be used in a generic sense, regardless of whether the substance is added to yield brighter, smoother, or harder deposits.) The production of bright deposits of metals such as copper and nickel, which would otherwise require buffing, represents an economy in the cost of both the buffing operations and the metal that would have been removed by buffing. With metals like zinc and cadmium which are not usually buffed, and which rapidly turn dull in normal atmospheric exposure, the production of bright deposits is justified principally by their initial appearance. (The use of bright dips for zinc and cadmium is to some extent a substitute for bright plating of these metals but is also associated with improving tarnish resistance.)

The large amount of industrial research on bright plating, especially of nickel, has resulted in the commercial application of several types of baths that are now extensively and successfully used. Control of

these baths is usually more critical than control of plain baths, especially if it is necessary to plate irregularly shaped articles on which the current density varies widely. For this reason certain "semi-bright" baths are frequently employed which yield deposits that require only light buffing. Apparently certain of these baths have a "smoothing" action;^{13,14} that is, the deposits produced on a dull surface (e.g., one with a profilometer reading of $20 \mu\text{-in.}$) become smoother as the thickness is increased. In contrast, most plating baths, such as the acid copper or Watts nickel bath, yield increasingly coarser deposits as the thickness increases. No adequate explanation of this smoothing action, or of its relation to brightening, polarization, or throwing power, has yet been presented.

The increased use of definite chemical compounds as addition agents may be expected to lead ultimately to a better understanding of their functions (e.g., of the individual groups in certain organic compounds). Thus far, however, no comprehensive explanation or theory of the action of these addition agents has been proposed. It is well known that many of the bright nickel deposits are laminated, probably as a result of a cyclic process in which, in the cathode film, the potential builds up to a point where the addition agents (or products derived from them) are codeposited with the metal, after which the potential decreases to some lower (less negative) value. Although oscillograph measurements have confirmed the existence of such cycles in the potential and current, these have not yet been closely correlated with the thickness of the laminæ or the constitution of the addition agents.

The presence of carbon in deposits produced from baths containing organic compounds is well known. It is not so generally recognized that such deposits may also contain sulfur or nitrogen, derived from the addition agents, and hydrogen, oxygen, sulfate, and chlorine, derived from the salts or water. Present analytical methods are inadequate for determining the composition of the actual compounds included in the deposits, much less their form or distribution. An important point is that the inclusions of foreign substances have a direct relation to the structure and physical properties of the deposits. Further studies are needed to throw light on such questions as the effect of the addition agent upon the cathode polarization and upon the composition, structure, and properties of the deposit, and upon the mechanism by which these effects are produced.*

SURFACE TENSION

The measurement and control of the surface tension of cleaning, pickling, and plating solutions is assuming an increased importance.

In the use of alkaline cleaners and emulsion cleaners, surface tension largely determines the formation and stability of the emulsions which result when most of the grease and dirt is removed. However, when such a solution is successfully compounded, its surface tension is usually within the desired limits, and its further measurement and control are unnecessary.

"Wetting agents" or "surface-active" substances in pickling solutions yield a foam blanket that decreases the spray. They also increase the assurance that the metal surface will be uniformly wet and acted on by the pickling solution. Such additions do not, however, excuse or justify inadequate cleaning of the surface prior to pickling.

In plating baths the surface tension has a direct relation to the tendency for pitting to occur, because it affects the size of the hydrogen bubbles that can be retained on a given surface. In general, a decrease in surface tension favors the release of bubbles and hence retards pitting. The extensive use of hydrogen peroxide in plain nickel baths depends on its ability to oxidize such impurities as ferrous iron and certain types of organic matter that may foster pitting. If an excess of hydrogen peroxide is present, it is reduced at the cathode, as indicated by a lower cathode efficiency for nickel deposition. Any residual hydrogen peroxide increases the stress in the deposited nickel.

Because hydrogen peroxide may oxidize some of the organic brighteners in nickel baths and thus destroy their usefulness, it is now customary to add wetting agents to bright plating baths to prevent pitting. Their effective concentration is most readily controlled by measurements of surface tension.

Most of the modern wetting agents are salts of organic sulfonic acids. In the insecticide industry alone, more than one hundred such compounds have been used to facilitate wetting of foliage by the sprays. Most of these compounds would probably reduce the surface tension of a nickel bath, but only a small number are compatible with the other required bath properties, such as a specific pH. Since these substances are complex and are generally used in small concentrations, their direct analytical determination is difficult, if not impossible. Most wetting agents lead to an increased brittleness of the nickel deposits, and care must be exercised to select those that have the minimum embrittling effect.

In most of the methods for measuring surface tension, direct comparison is made with pure water. At 20°C the surface tension of pure water is approximately 73 dynes/cm, and at 100°C it is about 59

dynes/cm. Roughly, the surface tension of water decreases about 1 dyne/cm for each rise of 5°C in temperature.

The common methods of measuring surface tension depend respectively upon: (a) the rise of the liquid in a capillary tube, (b) the size of the drop that falls from a horizontal annular surface, (c) the pull required to detach a circular ring of wire from the liquid surface, and (d) the sessile bubble method, in which the shape of a drop on a glass plate or of a bubble under the plate is measured.¹⁵

Of these methods, (b) and (c) are most conveniently applied to cleaning or plating baths. Method (d) is useful if surface-active agents are present, in which case some time may elapse before an equilibrium surface tension is reached. For method (b), sometimes called the drop-weight method, a stalagmometer is used. This consists of a glass tube having an expanded portion with a definite volume between two marks, and an attached capillary tube with the lower tip ground flat and polished. The number of drops of the solution corresponding to the measured volume is compared with the number of drops of pure water at the same temperature. Method (c), the tensiometer method, is usually applied by means of the DuNouy tensiometer, in which a ring of cleaned platinum (or platinum-iridium) wire is withdrawn from the surface of the liquid by applying torsion to a wire connected to the ring. The required load, measured in divisions on a circular scale, is compared directly with the load required for pure water at the same temperature.

VISCOSITY

An increase in viscosity of a plating solution affects the cathode polarization by retarding the upward movement of depleted solution on the cathode surface, the replacement of the cathode film by mechanical convection, and the diffusion rate of the depositing ion. In general, an increase in viscosity makes the cathode film thicker and hence raises the cathode polarization. This in turn may increase the throwing power. For example, in a "high sulfate" nickel bath the increased cathode polarization and throwing power are the result of the increased viscosity of the solution, as well as of the common ion effect of the sodium sulfate.

In electropolishing, relatively viscous solutions retard the replenishment of the solution entrapped in the depressions and thereby favor anodic solution of the projecting parts where the solution is more readily replenished. The viscosity of a plating bath has a direct relation to drag-out, because it determines the rate at which the solution drains from the object after its removal from the bath.

Although it is often helpful to know at least the relative viscosities of plating solutions, it is unlikely that routine measurements of viscosity would be useful for control. In most baths appreciable changes in viscosity will occur only if there are large changes in composition or concentration which can be readily determined by chemical analysis.

MECHANISM OF ELECTRODEPOSITION

No marked progress has been made in recent years on the mechanism of electrodeposition, even from simple salt baths. The present knowledge on this subject and the results of recent studies are summarized in a symposium on "Electrode Processes" held by the Faraday Society in 1947.¹⁶

Where and how a cation combines with an electron from the cathode to form a metal atom have not yet been established. At least two processes have been suggested. According to one theory the ion is preferentially neutralized and discharged at some point on the cathode surface that fills a gap in, or continues, an existing space lattice of the deposited metal. If no such point exists within a distance of the particular ion such that the available potential is adequate to cause discharge of the ion at that point, a nucleus of a new crystal lattice is formed. This theory postulates a slightly lower potential to cause growth of an existing crystal than to start a new crystal. According to the other theory the ions are neutralized and discharged at random on the cathode surface, and later the atoms orient themselves into the space lattice and crystal size that are characteristic of the metal. This theory involves the assumption that the discharged metal atoms have an appreciable initial mobility.

Any adequate theory of electrodeposition should not only account for the ion discharge and crystal formation at the cathode but should also correlate these with the prevailing polarization. An increase in cathode polarization usually leads to the formation of finer-grained deposits, yet other factors undoubtedly affect the crystal size and type. The problem becomes still more involved if metal deposition takes place from complex salt baths, in which most of the heavy metal is in the anions.

Although many methods of attack may prove fruitful, a more intensive study of the composition and behavior of cathode films probably will yield the most direct results. The methods proposed by Haring,¹⁷ Brenner,¹⁸ and Graham¹⁹ warrant further study, and especially Brenner's freezing method, which yields data on the concentration gradients but not necessarily on the composition of the salts or

ions in the cathode film. The procedure is difficult and time-consuming, but its use in a systematic study of a few types of bath may be worth while. In this and other methods of studying cathode processes, tracer techniques may also prove helpful.

DISTRIBUTION OF THE CURRENT AND OF METAL DEPOSITS

The inclusion in many specifications of requirements for a minimum thickness of deposit on significant surfaces has emphasized the importance of securing as nearly uniform metal distribution as practicable. Except with a few simple geometrical shapes and systems, a uniform distribution of current over the entire electrode surface is not possible. The distribution of metal, which is the significant result, depends upon: (a) the distribution of the current, and (b) the respective cathode efficiencies at the prevailing current densities. If, over the current range involved, the cathode efficiencies are equal, the metal distribution is the same as the current distribution.

The actual (or secondary) current distribution in any system is the result of: (a) the primary distribution, which is a function only of the shape and dimensions of the system, and (b) the polarization. The primary current distribution is that which prevails in the absence of polarization.

PRIMARY CURRENT DISTRIBUTION

In a series of papers on the theory of the potential, Kasper²⁰ has demonstrated with mathematical examples how the current distribution may be computed in certain geometrical systems. Typical results are illustrated by diagrams in which the equipotential surfaces and the lines of flow (which are always normal to these surfaces) are depicted. These computations and illustrations show conclusively that in most cases the shape and dimensions of the system have far greater effects upon the actual current distribution in electrodeposition than any effect that can be brought about by changes in polarization or cathode efficiency.

POLARIZATION

The effect of polarization can be computed only by mathematical consideration of the shape of the polarization curve, the conductivity of the electrolyte, and the geometry of the entire system. In practice, even the direction of the effects of differences in polarization, conduc-

tivity, and cathode efficiency upon the metal distribution upon a particular object cannot be predicted unless their separate effects are all in the same direction. Otherwise, it is entirely possible that a change in operating conditions, and hence in the above three variables, may make the metal distribution more uniform on an object of one shape and less uniform on another.

SPACING OF ELECTRODES

Another important result of these studies is the ability to predict for certain systems the effect of the spacing of the cathodes with respect to each other and to the anodes. In general, whenever the anodes and cathodes are separated by such distances that the equipotential surfaces approach planes (i.e., straight lines in the sectional drawings), any further increase in the spacing has no appreciable effect upon the current distribution. This "optimum" spacing is often only a few times the diameter of the electrodes.

THROWING POWER

The numerous researches on throwing power since 1925 have had as their goal the direct measurement of the relative behavior of various solutions with respect to current and metal distribution, and the presentation of results by numbers whose values expressed the relative throwing powers of the baths. Methods like that of Haring and Blum²¹ and its various modifications, in which a rectangular box is employed, attempt to represent by linear conductors two or more parts of an article of any shape on which the primary current density varies, and to which the "effective resistances" therefore vary (inversely). When such devices were proposed, it was clearly understood that, in all systems except linear conductors, the actual resistances are not directly proportional to the distances. The importance of this distinction has not always been appreciated. Actually, as shown by Kasper, many real electrode arrangements more nearly approach cylindrical or spherical systems, in which the relations are not linear. The inadequacy of linear models is most evident in estimating the effects of polarization, in the correct computation of which the entire shape of the article must be considered, and not merely the positions or relations of two selected points such as are represented by the box.

Recently Hoar and Agar²² have made a critical analysis of the factors that influence the values of throwing power as measured in the

Haring cell. Their detailed conclusions confirm the general principles stated here.

It was also early recognized that any numerical values for throwing power obtained in the box will depend upon its absolute size as well as upon the ratio of distances. The most that can be expected from measurements in different boxes is that they will place different solutions in the same order, even though the numerical values will not be alike or even proportional. If the measured differences in throwing power are relatively large (e.g., between an acid and a cyanide copper bath, or between a nickel and a chromium bath), they can readily be predicted from known or measurable values of polarization, conductivity, and cathode efficiency. If, however, the differences between two baths are small (e.g., less than 5% on the customary scales), different-sized boxes might reverse the results, because changes in the above three factors might have different relative effects. In such a case the results obtained with any box would be less likely to represent correctly the relative metal distribution upon objects of widely different shapes.

Throwing power is not a single, measurable property of a solution. The chief value of measurements made in any device, such as a box, is pedagogical. Such measurements may be useful to indicate the order of magnitude of the differences between different solutions or conditions of operation. When such differences are found to be small, their actual values, however expressed, are not significant. The same considerations apply to other empirical devices in which a cathode of a certain shape is used, because then the results with two or more solutions (unless they are widely different) are not applicable to articles of entirely different shapes.

COVERING POWER

In certain methods, for example the bent cathode^{23,24} and the cavity scale,²⁵ the behavior of the solution is judged by the extent to which the cathode is covered. For convenience, this property is preferably designated covering power, which is related to throwing power and to the lowest current density at which metal can be deposited from the bath.

PLATING RANGE

Covering power is in turn related to the plating range. In a broad sense this term may include the entire range of current density at

which a metal can be deposited from a given bath under any conditions. It is, however, more properly restricted to the range within which deposits having certain desired properties may be produced. In order to avoid the necessity of making a series of measurements, Hull²⁶ developed a rectangular box with an anode perpendicular to the sides and an inclined cathode. The current density on the cathode varies inversely with the logarithm of the distance from the near end (where the current density is highest). This device may be used to study the current density range within which desired (e.g., bright) deposits may be obtained, and to determine the effect upon that range of a given change in composition or operating conditions. It may also be used to control the operation of a given bath; for example, by indicating the required amount of some addition agent that cannot be readily controlled by chemical analysis.

PROPERTIES OF ELECTRODEPOSITS

THICKNESS

Numerous researches confirmed by experience have shown that the thickness of electroplated coatings is the most important single factor in their resistance to wear and corrosion. This property is most logically expressed in terms of the minimum thickness on "significant" surfaces—areas that are visible and subject to abrasion and corrosion. The earlier specification of average thickness was justified principally because satisfactory methods for measuring the local thickness were not then available. At present the specification of average thickness is confined largely to coatings of metals such as silver and gold, the intrinsic value of which is an important consideration.

AVERAGE THICKNESS

Methods for determining the average thickness of plated coatings depend upon solution of the coating. If this solution is such that there is no significant attack of the basis metal, the loss in weight gives directly the weight of the deposit; from this weight and the area and density of the coating the average thickness may be computed. If the basis metal is attacked, the weight of the coating must be determined by analysis of the resulting solution. For most plated coatings, stripping methods have been devised that are quantitative within about 10%. (Usually they are also applicable for stripping defective coatings prior to replating.)

LOCAL THICKNESS

By Linear Measurement. (a) Microscopical Method.²⁷ The microscopical measurement of appropriate cross sections is the most direct and generally applicable method for measuring local thickness and is, hence, widely used in specifications, especially as the umpire method. It destroys the specimens tested and requires considerable equipment and experience. For coatings with thicknesses down to 0.0001 in. (2.5 μ) its accuracy is about $\pm 5\%$.

(b) Chord Method.^{28, 29} This method consists in just cutting through the coating on a curved surface with a flat file, or on a plane surface with a precision grinding wheel, and measuring the width of the cut, i.e., the chord of the arc. The coating thickness T equals $C^2/8R$, where C is the width of cut and R is the radius of curvature of the surface or the grinding wheel. This method destroys the coating, but usually the basis metal may be stripped, repolished, and plated. With thicknesses down to 0.0002 in. (5.1 μ) its accuracy is about $\pm 10\%$.

By the Rate of a Chemical Reaction. (a) Immersion Methods. The best-known immersion method is the Preece test, in which a zinc-coated steel article is immersed in an aqueous solution of copper sulphate (sp. gr. 1.186) for successive 1-minute intervals until an adherent deposit of copper is produced on the steel. It has been shown³⁰ that this method is not a very reliable measure of thickness, because the results are influenced by the type of zinc coating and by the shape of the article. It is chiefly useful for indicating the relative distribution of the coating.

(b) Spot Tests. In these tests one drop of a reagent is applied to the plated surface, and the time required for complete solution of the coating at that point is noted. The best-known example is the measurement of thin chromium coatings by application of one drop of concentrated hydrochloric acid. Both the temperature and the concentration of the hydrochloric acid³¹ must be closely controlled to secure an accuracy of $\pm 10\%$.

(c) Dropping Tests. For these tests a stream of drops of an appropriate reagent is allowed to fall onto the plated surface at a controlled rate, and the time required for penetration of the coating is noted. This method is especially useful for such metals as zinc and cadmium, which dissolve readily without becoming passive. In the original method³² a solution of iodine in potassium iodide was employed for cadmium coatings. Subsequently,³³ acidified solutions of ammonium nitrate were used for both zinc and cadmium coatings.

More recently,³⁴ a solution containing 26.8 oz/gal of chromic acid (CrO_3) and 6.7 oz/gal of sulfuric acid was found to yield sharper endpoints for zinc and cadmium coatings. With chromic acid one thickness factor may be used for different types of cadmium deposits, and another for zinc deposits, including electroplated, hot-dipped, and sherardized. These factors vary with the temperature at which the test is made. In general, an accuracy of $\pm 15\%$ may be secured.

(d) Jet Tests. In these tests³⁵ a continuous fine stream of the reagent is allowed to impinge on the surface until the coating is penetrated, as determined by observation when the stream is interrupted at intervals. This method has been especially recommended for nickel coatings, for which a reagent containing 40.2 oz/gal of ferric chloride and 13.4 oz/gal of copper sulfate is recommended. The factor depends upon the temperature. Some bright nickel deposits dissolve at the same rate as plain nickel, and others about 50% more rapidly.

(e) Electrochemical Methods. The thickness of a coating may be determined by measuring the time required for it to dissolve anodically at a specified current density. A recent example³⁶ is the measurement of the thickness of chromium coatings by making them anodic in a solution of trisodium phosphate and sodium sulfate. In general, an accuracy of $\pm 5\%$ was obtained.

Magnetic Methods. These methods, which are rapid and non-destructive, depend upon the facts that: (a) nickel coatings are magnetic, and (b) any non-magnetic coating upon a magnetic metal such as steel decreases the magnetic effects of the metal. Such effects may be measured by changes in either the attraction of a permanent magnet or the reluctance of a circuit that includes an electromagnet.

A permanent magnet is employed in the instrument called the "Magne-Gage," which was developed at the National Bureau of Standards,³⁷ and in similar instruments devised by Hoare and Chalmers³⁸ and by Richards.³⁹ Instruments with a permanent magnet may be used to measure the thickness of nickel coatings on brass or zinc base die castings. Nickel deposited under different conditions varies in magnetic properties, but, when heated to 400°C for a short time, all nickel coatings acquire the same magnetic behavior.

When there is a non-magnetic coating on steel, the attraction is reduced by the interposition of the coating. As nickel is less magnetic than steel, its thickness on steel may also be measured. By making measurements with two magnets, for which appropriate calibration curves have been prepared, it is possible to measure the thickness of both the copper and the nickel layers in composite coatings on steel.⁴⁰

These instruments are calibrated with plated coatings of known thickness, by means of which they should be occasionally checked. They are applicable to a plane surface and to a curved surface with a radius of curvature at least three times the diameter of the magnet. Under appropriate conditions the results are accurate within about $\pm 10\%$. On rough surfaces the results are less reliable.

Instruments in which variations in an electromagnetic circuit are used have been described in England by Tait;⁴¹ somewhat similar instruments are made in this country by the General Electric Company. A similar device was also developed by Elwood⁴² for measuring non-magnetic coatings on steel.

X-Ray Methods. Isenberger⁴³ suggested that the intensity of the x-ray diffraction pattern might be used to measure the thickness of a plated coating. More recently, Wood⁴⁴ made efforts to measure the thickness of silver on plated spoons by means of the intensity of a radiograph. Neither of these proposals has resulted in a simple non-destructive method which is especially desirable for non-magnetic coatings on non-magnetic basis metals.

ADHESION

The adhesion of a plated coating is considered poor if the coating is detached when a stress is applied, for example, by deformation, change in temperature, evolution of gases, or corrosion of the basis metal through pores. Poor adhesion is likely to result from: (a) presence of some foreign material between the coating and the basis metal, (b) strains in the deposited metal, or (c) a weak layer of metal either on the surface of the basis metal or in the initial deposit. The last condition, which may permit some of the basis metal to adhere to the detached coating or vice versa, is evidence that then the adhesive force is at least equal to the strength of one or both of the members, which, strictly speaking, represents the best adhesion that can be measured.

In an effort to clarify the present confusion in terms used to describe the adhesion of coating, Faust^{45, 46} described and illustrated the various locations and types of detachment of a plated coating from a basis metal. He then proposed that the term "bond strength" be used to define the force necessary to detach a coating regardless of whether it separates at the metallic interface or within the coating or basis metal. The term "adhesive strength" would then be used to define the force required to detach the coating at the interface. As so defined, the bond strength may equal but not exceed the adhesive strength.

While such a distinction may at times prove advantageous, it would not eliminate the necessity of an explicit statement of the location and nature of the separation when a specific bond strength is reported. The adhesive strength as so defined would be incapable of direct measurement if it exceeded the strength of the coating and the basis metal. The subject needs further study before fully adequate terms can be defined.

The most conclusive evidence of the absence of any foreign material at the interface is the continuation of the size and shape of the crystals of the basis metal into the deposit, which may be of the same or of a different metal. The maximum adhesion might then be expected. This intimate contact of the basis metal and coating is most favorable to the formation of an alloy at the interface. If this alloy is strong, it may increase the adhesion, but, if, as with copper on a zinc-base die casting, a weak, brittle alloy is formed, the apparent adhesion is decreased.

Ferguson and associates conducted Research Project 3 of the American Electroplaters' Society on the adhesion of electrodeposits. Their bibliography, considerations, and conclusions⁴⁷ show that there is at present no quantitative method for measuring the adhesion of plated coatings on finished articles of varied shapes. Hence qualitative tests such as bending, hammering, stretching, or chiseling are frequently applied. At best, such tests indicate merely whether the adhesion is good or poor. The two quantitative methods that have been devised both require the preparation of special specimens and are therefore chiefly useful in research on the effects of certain variables upon the adhesion.

JACQUET METHOD

In the method of Jacquet⁴⁸ a thick coating is applied to a flat strip so that one end of the coating can be readily detached and held in a suitable tensile machine. The force (e.g., in pounds per inch or kilograms per centimeter) required to pull the coating from a strip of definite width is measured. A fundamental objection to this method is that the force is not applied normal to the surface; hence the apparent adhesion changes with the thickness of the coating.

Mesle⁴⁹ used a modification of the Jacquet method to study the effects of different variables upon the adhesion of plated coatings.

OLLARD METHOD

In the method of Ollard⁵⁰ a very thick coating, for example 0.1 in. of a metal such as nickel, is applied to one end of a cylinder of brass or

steel. The deposit is then turned on a lathe to leave a sharp external shoulder, and a hole is drilled in the center. The specimen is so placed that the shoulder rests on a steel collar, and a load is applied to the center by a small plunger. From the force required to detach the ring of deposit, the adhesion (e.g., in pounds per square inch or kilo-grains per square centimeter) is computed.

Rochl⁵¹ made a critical study of Ollard's method for measuring the adhesion of nickel to steel and cast iron. He found that, in order to obtain reproducible and significant results, it was necessary to insure that the fracture occurred in tension and not in shear. For a nickel coating on steel the shear strength had to be made at least 1.3 times the tensile strength of the bond. This was accomplished by having the steel cylinder exactly 1.00 in. in diameter and supported in a collar or die that was 1.02 in. in diameter. The inside hole was 0.938 in. in diameter, and the plunger was 0.375 in. in diameter, with a rounded end. With a nickel coating at least 0.09 in. thick, the measured adhesion of the "hard" nickel on steel was 85,000 lb/sq in., which was slightly above the measured tensile strength of this nickel (78,000 lb/sq in.). The "adhesion" of nickel (over copper) on cast iron was only 7000 lb/sq in. and the fracture occurred in the copper layer. These results show that Ollard's method is a valuable research tool, but that it must be applied with special precautions in order to yield reliable values for adhesion.

PROTECTIVE VALUE

In most cases electroplated coatings are applied because they have properties different from the basis metal, especially greater resistance to tarnish, or because they protect the basis metal against corrosion. Even when appearance is a primary consideration, protection against corrosion is also significant. With a specified basis metal, coatings may be divided into two classes: (a) those that (in a given environment) corrode more readily than the basis metal, and (b) those that corrode less readily. With steel, these types are represented by: (a) zinc and cadmium coatings, and (b) practically all other plated metallic coatings. The distinction is less sharp with other basis metals.

EXPOSURE TESTS ON STEEL

Extensive exposure tests conducted jointly by the American Electroplaters' Society, the American Society for Testing Materials, and the National Bureau of Standards⁵² have shown that the protective value of either zinc or cadmium coatings on steel is practically proportional

to their thickness. In either rural or marine locations a thin coating [e.g., 0.0002 in. ($5.1\ \mu$)] of either metal furnishes considerable protection, but in industrial atmospheres, which are likely to contain both sulfur dioxide and sulfur trioxide, zinc and cadmium are rapidly attacked and dissolved. Under these conditions cadmium coatings fail more rapidly than zinc coatings of the same thickness.

The protective value of more noble coatings on steel (e.g., coatings of copper, nickel, and chromium) depends principally upon the freedom from porosity of the coatings, as these metal coatings themselves are not rapidly attacked, even in industrial locations. Practically, the best way to reduce the porosity of copper and nickel coatings is to increase their thickness. On the other hand, there is an optimum thickness of decorative chromium coatings, at approximately 0.00001 to 0.00003 in. (0.25 to $0.75\ \mu$). Thinner chromium coatings usually have more pores, and thicker coatings may have more cracks.

SPECIFICATIONS FOR PLATED COATINGS ON STEEL

The specifications for plated coatings on steel adopted by the American Electroplaters' Society and the American Society for Testing Materials⁵³ may be summarized as follows. Zinc and cadmium coatings of each type are defined solely in terms of the minimum thickness on significant surfaces. For the chromium finishes the minimum thickness of nickel or of copper plus nickel is specified; the final nickel must be at least 50%. In addition, a minimum thickness of 0.00001 in. ($0.25\ \mu$) of chromium is required on all types. Exposure for a specified period in the salt spray test without appreciable corrosion is also specified. The thickness of the chromium is determined by the spot test with hydrochloric acid, and that of the other metals by the microscopic method.

COATINGS ON BRASS

Coatings of a given thickness of nickel and chromium furnish better protection on copper and brass⁵¹ than on steel, probably because the basis metal is less rapidly attacked, and not because the coatings are less porous. In fact, to obtain complete protection of brass under severe conditions requires nearly as thick nickel coatings as are required on steel.

COATINGS ON ZINC

On zinc and zinc-base die castings, the required thickness of nickel and chromium⁵⁴ is about the same as on steel. A copper layer under the nickel somewhat reduces the protective value, but, as it is not

practicable commercially to apply thick coatings of pure nickel, an initial layer of copper is almost always used on zinc die castings, especially when bright nickel is subsequently applied. The salt spray test is useful to detect pores in nickel or chromium coatings on zinc.

POROSITY TESTS

It has been difficult to study the causes and effects of pores in electrodeposited coatings because no quantitative methods have been available for detecting and evaluating porosity. In Research Project 6 of the American Electroplaters' Society, Thon and associates⁵⁵ have compiled an extensive bibliography and review of the porosity of electrodeposited metals. They found that the ferroxyl test yielded unreliable results for porosity, even when the concentration of potassium ferricyanide was increased to 6.7 oz/gal, and that of sodium chloride was decreased to 0.2 g/l. As part of this investigation, a study is in progress upon the intrinsic permeability of electroplated coatings (e.g., of nickel foils that have been deposited upon, and stripped from, stainless steel). The rates of passage of air or other gases through these thin foils, in which no pores can be detected by light transmission, have been measured. In general, the results show that characteristic and reproducible permeabilities are being measured. These permeabilities are proportional to the pressure differences, and inversely proportional to the densities of the gases. They approach zero with nickel foils more than about 0.0002 in. thick.⁵⁶

It remains to be determined whether there is any relation between the intrinsic permeability of plated coatings and their protective value. Most of the available evidence indicates that the latter is partly dependent upon the presence (or absence) of actual pores that can be detected, if not accurately evaluated, by methods such as the following. However, corrosion of the coatings undoubtedly plays an important part.

Salt Spray Test. In the specifications mentioned above, the salt spray test is used principally as a measure of the porosity of nickel or composite coatings on steel or zinc. At best, it is a measure of the quality of the coating and not of its protective value in any given environment, except as such a relation has been established by experience.

Considerable progress has been made in defining the conditions for operation of the salt spray test so that reproducible results can be obtained. The rate of corrosion in the salt spray has been shown to be directly related to the rate of condensation of the fog or mist upon the surface tested. Accordingly, most recent specifications for the salt

spray test⁵⁶ provide for the measurement and control of the volume of liquid that settles on a horizontal surface per hour, as well as the density and purity of the salt solution and the temperature of operation.

Ferroxyl Test. The ferroxyl test for porosity of coatings on steel depends upon the application of a reagent containing a corroding agent, usually sodium chloride and potassium ferricyanide. The latter yields spots of Prussian blue wherever the steel is attacked through pores. The reagent may be applied as a viscous solution, a spray, or a moistened paper previously saturated with the solution. Published results show that the reagent is likely to attack the nickel coating and produce pores where none previously existed. To reduce this attack, it has been proposed to reduce greatly the concentration of either the ferricyanide or the sodium chloride. In one modification the paper contains only sodium chloride and is later "developed" by immersion in a ferricyanide solution.

In the light of the work of Thon referred to above, it is doubtful if this or any other porosity test thus far described is sufficiently reliable to include in formal specifications.

Hot Water Test. The hot water method⁵⁷ has also been used to detect pores in nickel coatings. In a comparison by Strausser⁵⁸ of various methods of detecting pores, good agreement was not obtained. In general, fewer pores were detected by the hot water than by other methods.

MEASUREMENT OF THE PHYSICAL PROPERTIES OF ELECTRODEPOSITS

One of the most significant features of electrodeposition is that, by changing the conditions of deposition for a given metal, wide changes in its structure and properties may be produced. A knowledge of the direction and magnitude of such changes is desirable, not only to achieve any desired results, but also to avoid production of deposits with variable or undesirable properties. Because the physical properties of a metal depend largely upon its structure, it might appear expedient to consider first the factors that determine the structure. On the other hand, most applications of plated coatings depend upon their physical (or chemical) properties, and the structure is of interest only in its effect upon these properties. Methods of measuring the physical properties of metals, particularly their tensile strength, elongation, hardness, and brightness, are therefore important to the plating industry.

Recent studies on the physical properties of chromium⁹ show the wide range of properties obtainable, and the close relation of these

properties to the conditions of deposition and to the content of oxygen (i.e., of basic material) in the deposits.

Similar studies on nickel are in progress under Research Project 9 of the American Electroplaters' Society. The bibliography and survey⁵⁹ and a progress report⁶⁰ show a wide range of properties of electrodeposited nickel. It is hoped that the correlation of these properties with the conditions of deposition and the structure and composition of the deposits will yield interesting conclusions.

Since discussion of the specific properties, e.g., of chromium and nickel, is more appropriate under the chapters on each metal, the discussion here will deal with general considerations.

TENSILE PROPERTIES

In order to measure the elastic limit, tensile strength, and elongation of an electrodeposit, it must be in the form of thin sheets or strips, detached from the metal on which they were deposited (e.g., chromium alloys). Sometimes the tensile specimens are merely rectangular strips, but specimens with reduced sections yield more reproducible results. The tests are readily made in any tensile machine with the appropriate range of loads. In general, for a given metal, the tensile strength increases as the crystal size is decreased. Because the initial layers of a deposit are usually more fine-grained than the subsequently deposited crystals (especially from simple salt baths), the measured tensile strength (per unit cross section) of a very thin deposit is usually greater than that of a thicker deposit. In specific cases the nature of the separating medium may influence the structure and properties of the deposit.

If a metal is very brittle, and especially if, like chromium, it may contain cracks, it is difficult to measure its tensile strength or elongation. With most electrodeposited metals, however, significant measurements may be made. These show that, with a relatively soft metal like copper, deposits having tensile strengths from 12,000 to 50,000 lb/sq in. and elongations from 5 to 35% may be obtained. With harder metals like iron and nickel the corresponding ranges are about 30,000 to 200,000 lb/sq in. and 2 to 30% elongation.

HARDNESS

Reliable and significant hardness measurements are difficult to make on electrodeposits because: (a) the concepts of hardness are neither simple nor definite; (b) the various methods employed may measure different properties; and (c) the results by any method are likely to be influenced by the hardness of the underlying metal unless the de-

posits are relatively thick. In the last case the properties are not necessarily the same as those of the thinner layers used in actual plating. Finally, there is no simple or direct relation between the measured hardness and the resistance to wear under specified service conditions. Hardness measurements are, therefore, seldom used for control of production, though they are valuable for research.

The most extensive measurements of the hardness of electrodeposits were made by Macnaughtan and associates,^{61, 62} who measured the Brinell hardness of numerous metals, and also their resistance to abrasion by emery paper. They obtained only a rough correlation between these two properties.

The Vickers method, in which a diamond point is used to indent the specimen, has been frequently employed to measure the hardness of electrodeposits. Recently⁶³ an apparatus designed to measure the "microhardness" of brittle materials was used to study chromium coatings on steel. The Knoop indentor is a diamond of pyramidal shape such that the indentation has a length (measured with a microscope) that is about 7 times its width and 30 times its depth. With this device the measured hardness (about 900) of the chromium coatings that were at least 0.001 in. thick was independent of the hardness of the basis metal. For this method the coating thickness should be at least 14 times the depth of the impression. For the regular Brinell tests of coatings, a thickness at least 7 times the depth of impression is usually specified. When the coatings are fairly thick, the indentations are preferably made in a cross section of the deposit.

Because the scratch hardness method yields scratches that are at least similar to those produced by abrasion, it is often suggested as a measure of wear resistance. However, because the results are not reproducible, especially with very hard coatings (which yield fine scratches), the method is not very satisfactory for plated coatings.

REFLECTING POWER AND BRIGHITNESS

The present great interest in bright deposits, especially of nickel, emphasizes the need of reliable measurements of brightness. A sharp distinction must be made between: (a) the total reflectivity of a metal surface, which is determined principally by the composition of the metal, and (b) its brightness, which is determined largely by the smoothness of the surface.

Reflectivity. The reflectivity of a metal depends upon the wavelength of the light. For the range of the visible spectrum, average reflectivities of 90 to 95% are obtained with silver and aluminum; with electrodeposited rhodium, about 72%; chromium, 66%; and nickel,

62%. The reflectivity of chromium is relatively high in the ultraviolet range.

Brightness. For a given metal the brightness may be expressed as the relation between the specular and the diffuse reflectance. Egeberg and Promisel⁶⁴ used a method in which a value of 100% represents a "perfect" reflector. They measured the specular reflection from a plane at 45 degrees, and the diffuse reflection at 5-degree intervals. They found that, for relatively bright surfaces, over 99% of the reflection was specular, and that it was difficult to measure the small differences between different specimens.

Springer⁶⁵ has expressed the brightness of polished and plated metals in terms of the proportion of the light that is diffusely reflected when the incident beam is at 45 degrees. He found a considerable difference in results, which depended upon whether the incident beam was parallel or perpendicular to the polishing lines.

Recently Ollard⁶⁶ described an apparatus in which only the diffuse reflection is measured and is related to the total initial light intensity, which is controlled and calibrated.

Studies are now in progress at the National Bureau of Standards in cooperation with a subcommittee of A.S.T.M. Committee B8, in which an effort is being made to design and utilize equipment that will readily measure both the total reflected light and that reflected diffusely. If such methods prove satisfactory, the results for the difference (i.e., for specular reflection) should be independent of the composition and reflectivity of the metal surface. It will be necessary to determine whether these results are consistent with those observed by the human eye, which must be the ultimate criterion of appearance.

THE STRUCTURE OF ELECTRODEPOSITS

NATURE OF DEPOSITS

CRYSTALLINITY

All available evidence indicates that electrodeposits are crystalline. The state of crystallinity is somewhat different, however, from that of cast or worked metals. Electrodeposited metals are characterized, in general, by higher hardness, lower ductility, greater anisotropy, and finer-grain size, and may recrystallize with more difficulty than worked metals.

The surface appearance of electrodeposited metals may indicate the grain size of an electrodeposit, but usually only when the metals have

been deposited from simple or non-complex ion solutions. Metals deposited from cyanide solutions can appear very rough or coarse to the eye, but this roughness does not mean that the crystals are large. Actually, the crystals may be so small that they cannot be resolved under the microscope, even at high magnifications. The roughness in such cases is due to nodular growth, whereby the submicroscopic crystals grow radially from impurities to produce an overall macroscopic appearance of roughness. It is important, therefore, that discussion of crystal size be limited to results obtained from actual crystal size measurements as from microscopical cross-sectional examinations or x-ray investigations. There is much carelessness in the literature in descriptions of crystal size in statements about the fineness or coarseness of the "crystal structure" made after mere visual examination of the deposits.

Because the crystal size is influenced greatly by the substratum and also because electrodeposits are strongly anisotropic, statements regarding crystal size or shape should also mention the distance from the substratum and whether the observations were made parallel or perpendicular to the substratum.

Many factors influence the crystal structure of electrodeposits. Some of them are: solution composition (a very important factor), current density, degree of agitation, temperature, the presence of foreign agents, the geometry of the substratum, and the crystal size and structure of the substratum. The physical condition of an electrodeposited metal can be changed or controlled by varying the factors just mentioned. For example, copper can be deposited with a coarse, columnar, ductile crystal structure, from acid solutions, whereas when it is deposited from cyanide solutions the crystals will be submicroscopic and the copper will be harder, less ductile, and tougher.

Increasing the current density usually causes a reduction in grain size, an increase in hardness, and a lowering of the ductility. An exception to this principle may occur if there are present metallic impurities that may deposit out in greater concentration at low current density than at high current density, and thus cause a large increase in hardness or decrease in ductility. Agitation and an increase in solution temperature usually cause an increase in crystal size and ductility.

The small scale geometry of the basis metal can influence the direction of crystal growth, which is perpendicular to the fine scale structure of the surface. The crystal size of the substratum has a marked effect upon the crystal size of electrodeposits, particularly of those deposited from simple solutions such as nickel, copper, and iron. The

effects are more pronounced at low current densities (1.0 to 18 amp/sq ft) (see Fig. 1).

Impurities in the plating solution, both organic and inorganic, can affect the structure of the electrodeposited metal to a degree even greater than most of the factors just discussed. The presence, for



Fig. 1. Photomicrograph illustrating reproduction of the basis metal structure by an electrodeposit. The dark line on the bottom is the boundary between the base copper and the electrodeposited copper. Note that there is perfect extension of the crystal size of the basis metal by the electrodeposit. The dark line at the junction of the deposit and basis metal is not a void but is merely a difference in level due to differences in hardness between the basis metal and the electrodeposit. Magnification 250X.

example, of as little as 0.001 g/l of lead or silver in a cyanide copper solution can noticeably affect the structure of the deposit. These effects are different for various current densities, because of the varying ratio of copper to silver or lead plated out at different current densities. A study of the structure of deposits should be made with as pure solutions as it is possible to attain, and the operating conditions should be definitely maintained and recorded.

Electrodeposits may be one-phase metal deposits, metallic compounds, solid solutions, or they may have two or more separate phases. By variation of solution composition or conditions of deposition, single metals can be deposited in more than one phase if they are capable of

forming more than one phase. Electrodeposited cobalt was reported to have shown a mixture of two allotropic forms: the face-centered cubic and the hexagonal close-packed. The latter form is the usual one for cobalt. Wright, Hirst, and Riley⁶⁷ and others have shown that chromium can be deposited in both the body-centered cubic and the hexagonal close-packed forms. Body-centered cubic chromium is formed in the essential absence of trivalent chromium, whereas the amount of hexagonal form deposited depends upon the presence of trivalent chromium. The hexagonal form is changed to the body-centered form by heating at elevated temperatures.

Recently Snavely¹⁰ and associates have concluded that the reported hexagonal form of chromium consists of a chromium hydride. Brass deposits in the α -range have been shown to be solid solutions, and Kersten and Maas⁶⁸ found the x-ray structure of electroplated β -brass similar to that of the cast metal, except that the former showed less sharp lines. Stillwell and Feinberg⁶⁹ have shown that silver-cadmium alloys may be deposited as solid solutions or alloys, and that the stable phase, as determined by the equilibrium diagram, is the predominant phase in the electrodeposit. A metastable beta-phase has been shown to form at high current densities and temperature. Palatnik⁷⁰ reported that electrodeposited copper-nickel alloys are solid solutions, as would be expected from the equilibrium diagram for these metals.

Metals which do not have atomic diameters favorable for solid solution formation can be codeposited, but as two separate phases which usually appear as banded or layered deposits. Copper and lead make a typical example, and codeposits of these metals have been shown by Meyer and Phillips⁷¹ to be two alternately deposited phases of lead and copper. This subject will be discussed later.

Many electrodeposits are predominantly columnar in structure, owing to the anisotropic rate of crystal growth in which the vertical growth exceeds the horizontal or lateral growth. Sometimes the vertical growth is so rapid that marked acicular or needle-like deposits form as almost isolated crystals, and a weak, valueless coating results because of lack of lateral cohesion. Because of poor diffusion between these acicular structures, basic salts may form and deposit between the firmer metallic crystals. Glazunov⁷² has shown that this occurs in the deposition of silver from silver nitrate solutions. The columnar structures may be modified to conical or inverted conical structures, and, as will be shown later, the geometry of the substratum noticeably affects the structure of deposits.



Fig. 2. Photomicrograph of a cross section of a copper deposit made from a standard copper sulfate-sulfuric acid plating solution. The crystals are very large and are columnar in nature. The deposit was very soft. Magnification 100X.

Metals deposited from simple solutions usually are columnar in structure (see Fig. 2); these include copper, iron, nickel, and zinc. Other microscopic forms are the nodular and the horizontally banded. When horizontal banding occurs, the crystals may or may not be microscopically resolvable. Banded deposits are particularly characteristic of bright nickel deposits. Other types of structures of electrodeposits may be classed as disorganized and structureless. Chromium, and the metals deposited from cyanide solutions such as copper, cadmium, and silver, usually show no characteristic structure under the microscope; that is, the crystals appear to be unresolvable, although markings may be discerned which are frequently confused with true crystals.

GRAIN SIZE

Electrodeposited metals may possess grain sizes ranging from crystals large enough to be seen with the unaided eye to minute crystallites of the order of 50 Å in cross section. With certain exceptions, notably chromium, metals deposited from acid or simple solutions in the absence of foreign substances or addition agents have structures in which the crystals can be readily resolved under the microscope. Metals which deposit with relatively coarse structures from simple solutions are zinc, copper, lead, tin, cobalt, nickel, silver, and cadmium. All these metals, with the possible exception of lead, can be deposited from complex solutions, or from solutions containing addition agents, in crystalline forms so fine that they are unresolvable microscopically.

There is considerable doubt regarding the structure of chromium deposits. Symboliste⁷³ published photomicrographs of chromium deposits with structures resembling crystals, and which he believed were true crystals visible at 300 to 400 magnification. Meyer⁷⁴ doubted that these structures were really crystals, and he believed that these apparently individual crystals were composed of groups of finer crystals. Wood,⁷⁵ using x-rays, reported chromium deposits with grain sizes whose diameters were of the order of 8 to 14×10^{-7} cm. This would make the crystal diameters approximately 80 to 140 Å, a size which is well beyond the resolving power of the microscope. Meyer has noticed similar structures in cadmium and copper coatings deposited from cyanide solutions and, in spite of repeated attempts with many types of etching, he has been unable to resolve clear grain boundaries or grains. Of course, as shown later, there is considerable doubt about the validity of grain size determinations of electrodeposited metals by x-ray data.

PREFERRED ORIENTATION

Deposition of crystals with preferred orientation occurs frequently. The orientation is dependent upon such factors as the physical condition and composition of the substratum, current density, and presence of colloids. Wood⁷⁶ showed that nickel could be deposited upon copper up to a certain limit of current density, with orientations in the deposit, and that fiber-type deposits could occur or disappear as the current density varied. Finch and Williams⁷⁷ showed that the effects of the substratum may persist until the deposit is 30,000 Å thick.

Rubio⁷⁸ deposited zinc from a cyanide solution containing small amounts of nickel and licorice and found the (1120) axis oriented in the direction of the current flow (normal to the cathode). Palatnik⁷⁹ showed that zinc and cadmium deposited in the presence of colloids have oriented structures, the degree of orientation depending upon the concentration of the colloid. They also found that the brightness of the deposits depends upon the degree of orientation. Other workers have found preferred orientations in lead, nickel, and chromium deposits. One might expect that preferred orientation would tend to occur generally in electrodeposits, because of the highly anisotropic nature of the process, the direction of current flow and the diffusion restrictions.

In many cases bright plated deposits have been shown to possess preferred orientation, but all bright deposits do not necessarily have a "fibered" structure. A study by Read and co-workers⁸⁰ showed that for many plates a high degree of fibering is possible with dull as well as with bright deposits, and they could find no overall relationship between preferred orientation and brightness of the nickel deposits studied.

STRESS

That many electrodeposits are formed in a condition of stress has been known for many years. The tendency for an electrodeposit to curl or peel away from the basis metal, to crack, or to cause a thin basis metal to buckle, and the presence of twinning in the crystal structure are evidences of stress. X-ray patterns of electrodeposited metals often show broad and diffuse lines, and it is difficult to determine whether the breadth of these lines is due to the existence of extremely small crystals or to imperfection or distortion of larger crystals. In cold-rolling a metal, the lines generally increase in breadth up to a maximum which is characteristic of the metal. If the lines do not broaden, the crystals are already fully distorted. On cold-rolling elec-

trodeposited nickel,⁸¹ a marked increase was found in the breadth of the lines in certain deposits which indicated relatively little distortion in the original crystal. In other nickel deposits no increase in breadth was observed.

Cracking in electrodeposits is particularly noticeable when the stress is higher than the tensile strength of the deposit and the deposit is applied on a basis metal with physical strength less than that of the electrodeposit (e.g., chromium on brass, or nickel on lead). In the principal method of measuring stress in electrodeposition the extent of bending of a cathode of thin sheet metal, electroplated on one side only and fixed at one end, is noted. The extent of bending is a measure of the stress in the deposit.

Brenner and Senderoff⁸² described a spiral contractometer for measuring the stress of electrodeposited metals and discussed critically the computation of stress from such measurements. They also reported stress values for nickel deposits, chiefly from the Watts type of bath.

The stress may be either expansive or contractive, or there may be no stress at all. Nickel is deposited under great stress in the range of 5000 to 50,000 lb/sq in. from most types of solutions. In most cases the stress is contractive, and the magnitude is governed by many variables, such as temperature, *pH*, composition of the solution, and presence of impurities.

Phillips and Clifton⁸³ found, for example, in their study of the Watts type of solution that increasing the nickel chloride concentration raised the stress, increasing *pH* from 2.5 to 5.3 increased the stress, and decreasing temperature resulted in an increase in stress except at a *pH* of 4. They found no significant effect of current density between 20 and 50 amp/sq ft. They also found that copper deposits from cyanide solutions were more highly stressed than those from acid solutions. Graham and Lloyd⁸⁴ found wide variations in stress of deposits from various copper solutions—variations from contractive stresses of 15,000 lb/sq in. to expansive stresses of the order of 5000 lb/sq in.

The mass of accumulated information on stress indicates that correlation of the stress in electrodeposits with any one factor is almost impossible. Actual measurements should be made for any particular solution concerned. There is no direct correlation between hardness and stress.

HARDNESS

Electrodeposited metals usually possess hardness values considerably greater than those of fully annealed metals and frequently greater

than those obtainable for the same metals by work-hardening. Metals which may be electrodeposited so as to be considerably harder than their work-hardened state are chromium, nickel, platinum, rhodium, and palladium. The hardness depends upon such factors as current density, temperature of the plating solution, presence of addition agents or foreign metals, nature of solution (whether simple or complex), and various anions and cations present. Thus, for example, potassium tends to harden, and chloride (added to sulfate baths) tends to soften, nickel deposits. Such cations as Na^+ , K^+ , Al^{+3} , Zn^{+2} , Ni^{+2} , Fe^{+3} , Co^{+2} , Cu^{+1} , and Cr^{+3} have been reported⁷³ to increase the hardness of chromium deposits. Some hardness ranges reported by Macnaughtan and Hothersall⁷⁴ are given in Table 1.

TABLE I. HARDNESS OF METAL PLATES

Metal	Type of Solution	Brinell Number	Brinell Hardness	Fully annealed	Work-hardened
Chromium	Chromic acid	400-950	70	...	
Platinum		606-642	47	97	
Rhodium		594-641	101	...	
Palladium		190-196			
		385-435	49	109*	
Nickel	Sulfate	125-420	70	300	
	Sulfate with organic colloids	up to 550			
Iron	Sulfate-chloride	140-350	69	148	
Copper	Acid sulfate	40-62	40	102	
	Acid sulfate with colloids	up to 130			
	Cyanide	130-160			
Silver	Cyanide	60-79	25	68	
Cadmium	Cyanide	12-22	20	34	
Zinc	Sulfate	40-50	33-40	52	
Tin	Stannate	8-9	4-5	...	

It has been reported⁷⁵ that hydrogen has no effect on the hardness of electrodeposited chromium. Hydrogen appears to have little effect on the hardness of other deposited metals, although it may seriously affect the ductility of the metals. The extreme hardness of electrodeposited metals may be due to the combination of several factors, some of which are small grain size, preferred orientation, presence of stress in the crystals, and the possibility of dispersed foreign substances distributed throughout the lattice (similar to the mechanism of the dispersed solute in the age-hardening of alloys).

Kasper⁸⁷ found that the content of oxygen (and hence probably of basic material) was higher in hard than in soft deposits of iron. Brenner and associates obtained similar results with nickel deposits^{12, 88} and chromium deposits.⁹ The effect of potassium and chloride on nickel deposits may be explained on the basis of their respective stabilizing and deflocculating of basic salts that may be included in the lattice.

Because of the anisotropic nature of electrodeposits, their physical properties, including hardness, vary with the direction in which they are measured. Cuthbertson⁹⁹ found, for example, the hardness of acid copper deposits to be 61 Brinell when taken parallel to the cathode and 46 Brinell when taken perpendicular to the cathode. Brenner and Jennings¹² showed that the hardness of nickel deposits may vary with thickness, being harder adjacent to the basis metal and becoming softer with increasing thickness of plate.

RECRYSTALLIZATION

Studies of the recrystallization of electrodeposits have enabled better understanding of their nature. Nickel deposits have shown the presence of basic matter by annealing at 1000°C in vacuo for 4 hr. The results of annealing depend upon the condition of the electrodeposit. Soft nickel deposits recrystallize, giving large equiaxial grains with clean grain boundaries. With harder deposits that have well-oriented microstructures, grain growth takes place chiefly in a direction at right angles to the plane of the deposit, lateral grain growth being slight, owing to the segregation of basic matter which inhibits diffusion along the grain boundaries. Hard deposits of nickel that have fine-sized but not well-oriented grains form small equiaxial grains on annealing and show globular material in the grain boundaries.

Coarse tin deposits have been found to recrystallize at 200°C into small equiaxial grains. Deposits of copper from acid sulfate solution were found to recrystallize at 900°C into large grains with no evidence of non-metallic material. Copper deposits from cyanide solutions, however, recrystallized into small equiaxed grains with a quantity of non-metallic matter visible in the grain boundaries.

Storey⁹⁰ studied the recrystallization of iron deposits and observed large amounts of hydrogen given off at 500° to 600°C, but did not observe a change in crystal structure until an annealing temperature of 900°C was reached. He found that fine deposits recrystallized more readily than coarse deposits and that the grain structures produced from fine deposits were finer than from coarse deposits.

FACTORS AFFECTING DEPOSITS

PHYSICAL FACTORS

Effect of Substratum. The substratum or basis metal upon which another metal is deposited influences the character of the deposit geometrically as well as crystallographically. The effects of both small scale size (0.001 to 0.005 in.) and the large scale geometry of the substratum have been beautifully shown by Portevin and Cymboliste,⁹¹ by Meyer,⁹² and by others. Projections, holes, cracks, and loose particles may act as centers of orientation of crystal growth. Where the deposits grow in columnar manner, the crystals will orient themselves normal to the small scale structure rather than normal to the general plane of the cathode. The intersection of systems of crystal growth may be discontinuous and, therefore, be a source of porosity in the deposit. Phillips,⁹³ Pinner,⁹⁴ and Baker⁹⁵ have all published data indicating that the type of polishing of the basis metal affects the corrosion resistance of metal deposited. However, with deposits of copper, nickel, and chromium on cold-rolled steel, Lux and Blum⁹⁶ found no appreciable effect of the polishing of the steel on the protective value in accelerated and exposure tests.

Meyer⁹² has shown photomicrographs indicating that ordinary concepts of throwing power are not valid for minute scratches (0.005 in. or less) which have considerable depth in comparison with width. Kasper⁹⁷ has discussed theoretical reasons for the occurrence of this phenomenon. Scratches have also been shown to create nodules in deposits from acid copper solutions, probably as a result of localized higher current densities at the projecting edges of the scratch.

Material projecting above the plane of the cathode as a result of preferential solution of part of the components of the cathode may affect the structure of the deposit. The effects of small scale geometry of the substratum are due to variations in at least three factors: (a) local current density, (b) diffusion, and (c) the crystallographic effects of the substratum.

Non-uniformity of the substratum may also markedly affect another factor met with in electrodeposition, namely, pitting. The work of Maughtan and Hothersall⁹⁸ showed that there is much less pitting in electrodeposits, particularly nickel, when the metal is deposited upon a metallurgically uniform surface, such as electrodeposited copper, rather than upon a heterogeneous surface such as

steel. However, pitting can result from factors inherent in the solution even when copper is the substratum. (See Fig. 3.)

Many workers have shown that the structure of the basis metal or substratum has an influence on the crystal size of the metal electrodeposited thereupon. Huntington⁹⁹ was one of the first to call attention to the fact that electrodeposited copper could be influenced by the

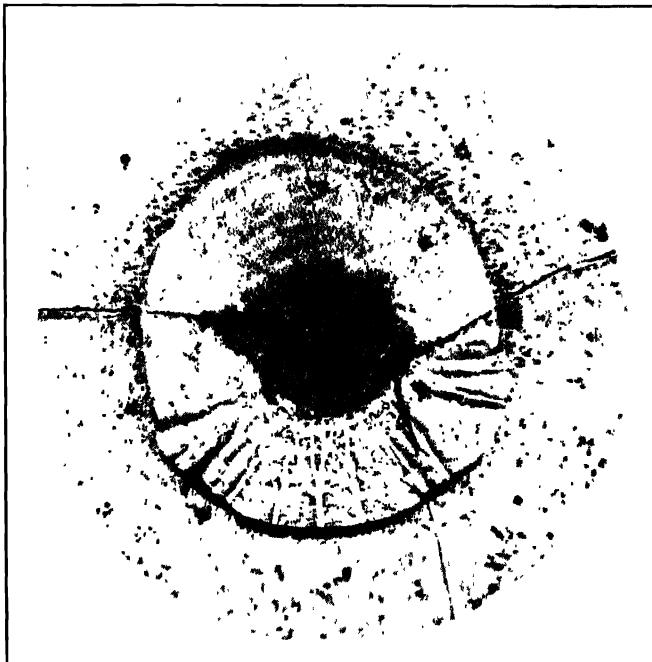


Fig. 3. Surface view of a typical pit in nickel plating. Note the concentric dark rings illustrating where hydrogen bubbles repeatedly formed and broke during deposition. Magnification 500X.

structure of the copper upon which it was deposited. In 1916 Hogaboomb¹⁰⁰ mentioned difficulties from coarse silver deposits traceable to the influence of the basis metal, and in 1921¹⁰¹ he pointed out that one of Blum's¹⁰² photomicrographs of alternately deposited metals showed reproduction of the rolled copper base in the electrodeposit. Later, Blum and Rawdon¹⁰³ published photomicrographs which clearly showed the extension of the crystal structure of the cast copper base by electrodeposited copper. Graham¹⁰⁴ repeated these observations for copper deposited upon copper, and he also was successful in obtaining similar results for copper deposits upon brass, but was uncertain of his results for nickel upon nickel. Hothersall¹⁰⁵ published a

photomicrograph of nickel deposited upon nickel in which the deposit reproduced the structure of the basis nickel. The most brilliant work in this field has been done by Hothersall,¹⁰⁶ who showed reproduction of nickel deposits upon nickel, tin upon tin, and tin upon antimonial lead. He was able to show reproduction of the crystal size of the basis metal by the deposit for metals in the same system with lattice parameters varying from 2.4 to 12.5%; and also reproduction between basis metal and deposits when they belonged to different crystallographic systems, e.g., tetragonal tin upon face-centered cubic copper, and copper upon β -brass, which has a body-centered cubic structure. Other workers have shown the reproduction of the structures of zinc upon zinc, cadmium upon cadmium, and lead upon lead. Tammann and Straumanis¹⁰⁷ reported extension of the crystal size of nickel by copper if the current density did not exceed 2 amp/sq ft.

In all the work that has been done, however, there does not appear to be a satisfactory answer to this question: Is the reproduction actually a pseudomorphic reproduction of the basis metal structure by the deposit, or is it merely reproduction of crystal size and of orientation? Finch and Williams,⁷⁷ using electron diffraction for determining the structure of nickel deposited upon copper, studied this problem and found that no pseudomorphism was indicated. They even cast doubt on the validity of microscopic observation as a means of detecting reproduction of the structure of the basis metal.

These workers and others report, as we would expect, that the extent of reproduction is dependent upon the crystal size of the substratum, large crystals having greater effects than small crystals. In addition, the type of solution, current density, and factors which influence the ratio of formation of crystal nuclei to crystal growth all influence reproduction. The type of crystallographic plane lying in the plane of the surface of the cathode may also affect the degree of crystal reproduction.

Many workers have shown that polished surfaces may cause orientation of thin layers of metals deposited upon them. It is common knowledge that thin deposits of nickel plated on a buffed surface will be bright, even from a Watts-type solution that ordinarily gives dull deposits. The first layers of metal, even up to a hundred-thousandth of an inch in thickness, take on the orientation of the basis metal. Meyer⁷¹ has published a photomicrograph illustrating this for copper deposited from an acid solution upon buffed nickel plate. A fine-grained structure was shown to persist until the deposit was 0.0005 in. (0.0125 mm) thick. Naturally, the extent of this reproduction of

the fine structure of the basis metal will depend upon factors such as current density, type of solution, and rate of agitation.

Evidence that metals may deposit to form exact continuation of the basis metal lattice is given by the perfect reproduction of twinning in a copper substratum which was reproduced by a copper deposit from an acid copper solution. Twinning involves a shift of layers of atoms a distance only a fraction of the lattice parameter, and it is interesting that this twinning arrangement of the atoms of the basis metal can be exactly reproduced by an electrodeposit.

In a recent paper Finch, Wilman, and Yang¹⁰⁸ reported a study by electron diffraction of the formation and growth of electrodeposited crystals. They concluded that the growth involves three stages: (1) an initial stage that is most affected by the substratum, (2) a transition stage, and (3) a final stage in which the structure is characteristic of the conditions of deposition.

Agitation and Temperature. In general, any condition tending to increase the supply of ions available for discharge at the cathode favors an increase in crystal size. Thus, for constant current density, agitation favors the formation of larger crystals. Likewise an increase in temperature favors the formation of larger crystals.

ELECTROCHEMICAL FACTORS

Type of Solution. Metals deposited from complex ion solutions are usually so fine-grained that the structure is unresolvable under the microscope. Salts or other substances that may lower ionization, e.g., by common ion effect, cause finer deposits to be formed. The most common type of complex ion solution is the cyanide solution; pyrophosphate, amine, and ammonia complex solutions are also being used.

Current Density. Higher current densities usually favor smaller crystal size. Frequent reports that the grain size is larger with an increase in current density may have been based upon visual observation. As has been mentioned earlier, deposits may look coarse owing to nodular growths, but these deposits may really be composed of very fine crystals.

BRIGHT DEPOSITS

The expression bright deposit refers to those which have high specular and low diffuse reflection, and does not refer to the amount of total light reflected or to the wavelength concentrations of light reflected. They are essentially plane surface deposits.

A common conception is that deposits, to be bright, must have a very small crystal size, less than the wavelength of light. However, it is understandable that a surface composed of coarse crystals can be smooth and bright. Jacquet¹⁰⁹ and others have produced, on coarse-grained metals by anodic "polishing" or smoothing, surfaces which had reflectivities greater than those obtainable on mechanically polished surfaces. It is conceivable that deposits can be bright, even with a relatively coarse grain, if the crystals are so oriented that their faces are essentially parallel.

Oriented structure appears to be a characteristic feature of many bright deposits. Palatnik⁷⁹ found from x-ray studies that the brightness of zinc and cadmium deposits increased with the degree of orientation of the crystallites. Kosolapov and Mett¹¹⁰ also found that the luster of zinc deposits increased with an increase in anisotropy. Wood⁷⁵ found both dull and bright chromium deposits to have crystal sizes of the same order of magnitude but found a decided preferred orientation in the bright deposits and not in the dull deposits. He also found that the brightness of nickel deposits increased with an increase in preferred orientation. In a paper on the structure of zinc electrodeposits, Fischer and Barmann¹¹¹ state: "Debye pictures showed that, for zinc deposits from alkaline solutions, a more or less pronounced fiber texture results; with deposits from acid solutions, an irregular structure was obtained. For the textured deposits, the (111) plane lies in the plane of the cathode surface. Bright zinc deposits are particularly fine grained, but they are not, as was formerly believed, smaller than the wavelengths of light. The high brightness of bright zinc deposits, therefore, must be attributed to their pronounced texture." As already mentioned, the existence of fibering or preferred orientation in an electrodeposit does not always imply that the coating will be bright.

It is believed that copper deposits from cyanide solutions are sufficiently fine-grained to be bright, and that their lack of brightness is due to improper orientation. Although the copper deposits cannot be resolved microscopically, the visible structure indicates that the crystals grow in a manner nodular or at least decidedly random. It was believed that this type of growth is caused by codeposition of basic material, because the cathode efficiencies are considerably below 100%. Maenzaughtan and Hothersall⁸⁵ found, by annealing copper deposits from cyanide solutions in vacuo, that non-metallic matter was present in the deposits. If this conclusion is true, copper deposits plated from cyanide solutions at 100% cathode efficiency should be bright or nearly bright. This has been found in a commercial copper

solution recently developed. Deposits from a complex amine copper solution¹¹² also are bright, and these deposits are formed with 100% cathode efficiency.

The foregoing discussion does not imply that preferred orientation is the sole criterion for brightness; this is definitely not true. Preferred orientation appears to be an important factor for brightness of

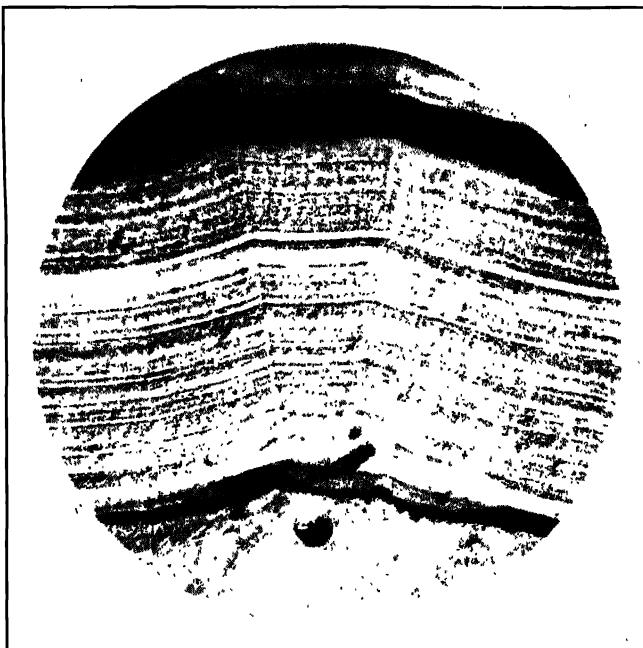


Fig. 4. Banded structure of a bright nickel deposit. These banded structures are characteristic of most bright plating solutions. Magnification 500X.

deposits, but no data appear to be available which correlate crystal size and degree of orientation for various metal deposits.

As mentioned on page 7, the role of addition agents in producing bright deposits is still not clear. Meyer is convinced that no one theory applicable to all cases will be found. It appears, for example, that so-called brightening agents may or may not be codeposited with the metal. Meyer and Phillips⁷¹ have expressed the opinion that, for metals acting as brighteners, the profound effects produced can only doubtfully be attributed to lattice interference effects of the metal itself. It has been suggested that these profound effects may in some cases be due to codeposition of these metals as basic salts or oxides. A study of the precipitation pH of metals, and espe-

cially of the higher alkalinity of the cathode film, lends credence to this hypothesis.

Many bright deposits on the market exhibit horizontal striations or banding in microscopic cross section. This is particularly true for most bright nickel deposits (see Fig. 4); and the condition has been observed in copper deposits brightened by lead or cadmium. The banding may have several causes. Obviously, the deposits are not homogeneous. The condition may be due to alternate deposition of differ-



Fig. 5. Photomicrograph of a deposit from a cyanide copper solution containing 0.1 g/l of lead. Note the banded structure representing alternate deposition of lead and copper as well as the pronounced nodule formation. Magnification 500 \times .

ent-sized crystals or to alternate deposition of two phases, either of allotropic modifications of the same metal (a rare condition) or of alloys, or to deposition of metal and another metal, oxide, basic matter, or adsorbed organic matter. Apparently, under normal conditions of deposition, the first layers of atoms formed are always oriented by the substratum. Thus a mechanism of bright deposit formation could be the alternate deposition of metal and foreign substance with preferred orientation occurring in the metal deposit.

In the codeposition of copper and lead, it is difficult to believe, because of the decidedly unfavorable atomic size factors, that lead can make regular entry into the copper lattice. For this case alternate

deposition of lead and copper has been shown to take place with noticeable banding (see Fig. 5) and brightening of the deposit.

Many brighteners, particularly organic brighteners, contain polar substances, or they may be reduced to simpler substances which can be absorbed in the electrodeposit to cause a banded type of structure, which usually leads to brightness. Materials that are highly adsorbed at metal interfaces, and surface-active materials, are extensively used as brighteners in nickel plating.¹¹³ Taft and Horsley¹¹⁴ found a correlation between surface activity of organic acids and their brightening effects on silver deposits from silver nitrate solutions. The accurate analytical work of Taft and co-workers¹¹⁵ and other studies indicate that brightening materials can be codeposited with the metal or can be adsorbed, as Jaquet's¹⁰⁹ studies indicate. Hence, one mechanism for bright plating in the presence of organic brighteners may be alternate deposition of metal and deposition or absorption of brightener, a reduction product of the brightener, an oxide, a metal sulfide, or another metallic phase. It should be pointed out that many substances that appear to be non-polar may, after being added to the plating solution, actually form polar substances by oxidation, reduction, or hydrolysis.

Other mechanisms may result in bright deposit formation. Simple columnar growth such as has been observed for bright zinc deposits from alkaline solution may result in bright deposits. A certain smallness of grain size will be necessary for brightness, even with columnar growth.

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2.

Methods of Control

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Every electroplater is well aware of the fact that the successful operation of his plating processes depends upon both art and science. In practice the experienced electroplater relies upon observations, empirical data, and scientific tests, in addition to specific formulation and the normally controlled plating variables such as temperature. It is becoming increasingly important with the advancements in bright, smooth, single-metal and alloy deposition that the successful operation of any complex plating process include a number of rapid tests on both the electrolyte and the deposit. More rigid specifications for electrodeposits increase the need for the electroplater to know more about the bath and the deposit obtained on the cathode from piece to piece, with the result that rapid tests, theoretical or empirical, are important to maintain uniform quality. Unfortunately, a number of the most valuable tests are entirely empirical in character and are valueless unless each operator develops a background of experience on his particular processes and product. This chapter describes briefly some of these tests and their significance in specification plating. The chapter is divided into two parts: control of the electrolyte, and control of the deposit.

CONTROL OF THE ELECTROLYTE

MEASUREMENT OF *pH*

The determination of the hydrogen ion concentration of a plating bath is usually very important in the control of its performance. Since small concentrations of hydrogen or hydroxyl ions involve negative exponents which are inconvenient to use, Sorenson¹ in 1909 suggested a simple numerical scale, which he designated *pH*, to replace

* Cleveland Graphite Bronze Co., Cleveland, Ohio.

the exponents with single-digit positive numbers by the following relationship:

$$pH = \log \frac{1}{C_{H^+}}$$

where C_{H^+} is the molal hydrogen ion concentration.

The pH scale ranges from 0 to 14 numerically. On this scale 7 is neutral, values below 7 indicate acidity, the degree of which increases with decrease in number, and values above 7 measure alkalinity, the degree increasing with the numbers. It is important to note that pH is a measure of the degree of acidity or alkalinity rather than of the amount of acid or alkali present.

The development of the thermodynamic activity concept has led to a slightly different definition of pH, but the fundamental character of the pH unit is unchanged. The term activity, designated a_{H^+} , may be defined as a corrected concentration so that the equilibrium constant is a true constant. For very dilute solutions, activities and concentrations are essentially equal, whereas for higher concentrations the activity of the ion becomes progressively smaller than the total concentration of the ion. The measurements of pH are most significant between 2 and 12; outside these limits pH values may be very misleading. Since a very small volume of the common mineral acids or bases changes the pH of a given solution very rapidly, it becomes necessary for buffer solutions to be used as pH standards. They are solutions which resist pH changes and are almost invariably a mixture of a weak acid or a weak base and their salts. Buffers listed by Glassstone² for the range pH 2.2 to 12.0 are given in Table 1. Most of

TABLE 1. BUFFER MIXTURES *

	pH Range
Phthalic acid and potassium acid phthalate	2.2-3.8
Phenylacetic acid and sodium phenylacetate	3.2-4.9
Potassium acid phthalate and dipotassium phthalate	4.0-6.2
Sodium dihydrogen phosphate and disodium hydrogen phosphate	5.9-8.0
Boric acid and borax	6.8-9.2
Diethylbarbituric acid and sodium salt	7.0-9.2
Borax and sodium hydroxide	9.2-11.0
Disodium hydrogen phosphate and sodium hydroxide	11.0-12.0

* From Reference 2.

the common plating baths, especially the alkaline baths, exhibit sufficient buffer action so that pH measurements in the recommended range are usually satisfactory.

The measurement of *pH* is subject to a number of additional errors³ such as salt, protein, temperature, improperly buffered solutions, and specific errors due to reaction between ingredients as the indicator in colorimetric methods or the quinhydrone in electrometric methods. Fortunately, these errors vary with different methods, and usually *pH* determination methods can be chosen so that the sources of error largely cancel out. It is recommended that several methods be employed and checked against each other for each specific bath, if accuracy greater than ± 0.1 *pH* is required, and that the most reproducible method be used for future determinations.

Table 2⁴ gives the a_{H^+} and *pH* for some of the common acids and alkalies used in industry.

TABLE 2. ACTIVITIES AND *pH* OF TYPICAL ACIDS AND BASES⁴

Solute	Moles per Liter	a_{H^+}	<i>pH</i>
Hydrochloric acid	1.0	8.0×10^{-1}	0.1
	0.1	8.5×10^{-2}	1.07
	0.01	9.6×10^{-3}	2.02
	0.001	9.7×10^{-4}	3.01
Sulfuric acid	0.05	5.9×10^{-2}	1.23
Acetic acid	1.0	4.3×10^{-3}	2.37
	0.1	1.3×10^{-3}	2.87
	0.01	4.3×10^{-4}	3.37
Ammonium hydroxide	1.0	1.7×10^{-12}	11.77
	0.1	5.4×10^{-12}	11.27
	0.01	1.7×10^{-11}	10.77
Sodium hydroxide	1.0	8.9×10^{-15}	14.05
	0.1	8.5×10^{-14}	13.07
	0.01	7.6×10^{-13}	12.12

* From Reference 4.

The methods for *pH* measurements fall into two classes, namely the colorimetric or indicator methods and the electrometric methods.

COLORIMETRIC METHOD

The colorimetric method is a simple and inexpensive method of determining *pH* with a medium degree of accuracy, and is based upon the fact that the colors of certain organic compounds correspond to a definite *pH*. The colorimetric method for plating solutions usually involves only small errors,* except for poorly buffered baths and some

* Mention might be made of the fact that certain of the colorimetric standards for *pH* determination on the market include a salt error of 0.4 to 0.5 *pH* unit. This does not destroy their usefulness, but allowance must be made for this error.

metals or salts which react with the indicator. Since there are a large number of indicators,* a check with a different one or by an electrometric method will establish the accuracy of the indicator method. In very highly colored solutions, the accuracy of this method may be questionable. In general, the use of indicator pH papers involves a slightly higher error in practice than indicator solutions. For most applicable solutions, the indicator method will give a pH accuracy of from 0.05 to 0.1 unit. In order to obtain this accuracy, a definite amount of the unknown solution is taken and the color compared with those produced at the same concentration, in a series of buffer solutions of known pH. By matching the colors, the pH of the unknown becomes apparent.

ELECTROMETRIC METHOD

The principle of determining pH by electrometric methods is based on the fact that certain pairs of electrodes in contact with a given solution acquire an electrode potential (emf) which depends on the hydrogen ion concentration. When one of the electrodes is of known potential, the pH can be readily calculated. The reference electrode most commonly used is a saturated potassium chloride-calomel electrode which has a potential of +0.2458 v at 25°C with respect to the standard hydrogen electrode. See Table 3. The emf of the combina-

TABLE 3. STANDARD REFERENCE ELECTRODES VERSUS THE STANDARD HYDROGEN ELECTRODE TAKEN AS ZERO

Half-Cell	$E_{25^{\circ}\text{C}(77^{\circ}\text{F})}$, v
0.1 N calomel	0.333
1.0 N calomel	0.280
Saturated calomel	0.246
Silver-silver chloride	
Chloride ion unit activity	0.222
0.1 M KCl	0.288

tion in a given solution is measured with a potentiometer (a very accurate voltmeter), and the pH is then calculated by means of the emf equation applicable to the particular electrode used. Although a great variety of electrodes has been used in research, only the hydrogen, quinhydrone, antimony, and glass electrodes are used in industry.

in comparing the pH values obtained by their use with pH values obtained in other ways.

* Reference 3, pp. 76-90.

All the limitations of any given electrode should be considered before its selection for any application. The known sources of error of each type should be avoided. After a definite type has been selected, the two most important variables encountered are temperature and junction potential.

For each of the three oxidation-reduction electrodes described, with a calomel electrode as reference, the following relation will exist:

$$pH = \frac{V - v \text{ or } (\Delta E)}{0.0001983T}$$

where V is the voltage measured by the potentiometer, v is the potential of the calomel at a given temperature, and T is the absolute temperature. The temperature corrections for the saturated calomel electrodes are listed in Table 4.

TABLE 4. TEMPERATURE CORRECTIONS FOR SATURATED CALOMEL ELECTRODES

Temperature	Millivolt Correction per pH Unit
0°C (32°F)	54.2
25°C (77°F)	59.1
70°C (158°F)	68.0

In addition to the potentials at the two electrodes, there is a third potential if two different solutions are in contact with each other. The difference of potential set up at the junction of the two solutions is caused by the difference in the rates of migration of the ions. As is common practice, the calomel half-cell is employed as the reference electrode for electrometric pH measurements. It consists of pure mercury in contact with a mercury and mercurous chloride paste. In order to minimize the junction potential, connection is made between the electrode and the solution through a salt bridge of potassium chloride. Potassium chloride is used in the bridge because the transference numbers of the two ions are approximately equal. In order to minimize leakage, mechanical devices such as gelatin plugs and loosely fitted glass joints are frequently employed.

The Hydrogen Electrode. The chief value of the hydrogen electrode is that it is the standard for all electrometric pH measurements (arbitrary value 0.000 v), and against which all other methods are checked.* It consists of an electrode of platinized platinum foil immersed in the solution to be tested, with hydrogen gas bubbling around the elec-

* Reference 2, pp. 993-994.

trode to keep hydrogen adsorbed on the surface. Because it is so inconvenient to use, slow to reach equilibrium, and is so easily poisoned by a variety of substances, it is not suitable for practical *pH* measurements.

Quinhydrone Electrode. If a platinum or gold wire is immersed in a solution that is saturated with quinhydrone,⁵ a slightly soluble organic compound which maintains in solution equimolecular weights of hydroquinone and quinone, it acquires a potential that mathematically reduces to

$$pH = \frac{0.4538 - E}{0.059} \text{ at } 25^\circ\text{C}$$

where *E* is the observed potential referred to a saturated calomel electrode.

The quinhydrone electrode is excellent for measurements in the range of *pH* 0 to 7. It is simple and convenient to use, is not easily poisoned, and develops its potential rapidly. Above *pH* = 8.5 the alkali reacts chemically with the quinhydrone so that the voltage is no longer a linear function of *pH*. It is also unreliable in the presence of oxidizing or reducing agents and in solutions containing appreciable quantities of salts or proteins.

Antimony Electrode. The antimony electrode⁶ is simply set up by inserting a rod of cast antimony in the experimental solution and measuring the emf in combination with a saturated calomel reference electrode, the mathematical relationship being

$$E = -0.008 + 0.059 \text{ pH}$$

The useful range of the electrode is between *pH* 2 and 7, and even within these limits previous calibration against a set of known buffers is necessary. It cannot be used in the presence of active oxidizing agents, and serious errors result in the presence of certain cations, such as copper or silver, or substances that form complex ions with antimony, such as tartrates or citrates.

Glass Electrode.^{7,8} One of the most important types of electrode for practical purposes is the glass electrode. This electrode operates on the principle that, when a thin membrane of suitable glass separates two solutions of different hydrogen ion concentrations, a measurable potential is observed. The resistance of this glass membrane is high so that a very sensitive vacuum tube potentiometer must be used

to measure the voltage. The electrode consists of a glass bulb or tube inside of which is a suitable solution and reference electrode of constant potential; hence the net potential is dependent solely upon the pH of the outside solution being measured. The glass electrode and a calomel reference electrode connected through the external circuit are immersed in the solution.

The glass electrode can be used in the presence of oxidizing or reducing agents and in unbuffered solutions. The main disadvantage is its unreliability in solutions of high sodium ion concentrations. The ordinary glass electrode in the presence of sodium ions has a useful pH limit of approximately 9. Mention should be made of the fact that, in the absence of sodium ions, it can be reliably used for alkalinites above this value. However, an E-type glass electrode has been developed for use in the range of 9 to 13 pH in solutions of appreciable sodium ion concentration.

Modern pH meters are designed for convenience and accuracy. Adjustments are made against a known buffer solution, and the pH of the experimental solution can be read directly from the calibrated potentiometer dial. Temperature correction tables are unnecessary because of the temperature compensator for the range of 10° to 40°C.

SIGNIFICANCE OF pH IN PLATING

The control of pH in a plating solution is necessary primarily to maintain the desired performance of the bath and the quality of the deposits. Most plating baths operate at an optimum pH range found empirically to produce and maintain high production standards. If the hydrogen ion concentration is not properly controlled, the bath may not operate at optimum efficiency, or the physical properties of the deposit may be affected. For example, iron or nickel deposits may become pitted, cracked, or curled, or zinc may become spongy or porous, when deposited in the presence of excessive acidity. In general, pH measurements have little practical value for baths operating at high acidity or alkalinity. In baths where pH control is necessary, a precision of ± 0.1 is usually more than adequate.

MEASUREMENT OF SURFACE TENSION

The increased use of wetting agents in electroplating solutions makes it desirable in many cases to measure and control the surface tension.

Wetting agents are sometimes used in alkaline cleaners, in pickling solutions, and as anti-pit agents in plating baths. All effective wetting agents cause a sharp drop in surface tension for very small concentrations with very little, if any, further change at increased concentrations.

The relation of surface tension to the emulsifying properties of alkaline cleaners is well established; however, the variations in chemical and physical properties of the cleaners and their role in removal of grease and oil are far more complex than any simple correlation between the surface tension and the efficiency of a cleaning solution. These determinations represent merely one factor in control which may lead to greater efficiency or uniformity of operation. Some wetting agents appear to be of value as anti-pitting chemicals because they promote rapid removal of gas bubbles from the cathode.

The surface tension of a liquid is measured by the perpendicular force that it can exert upon a straight line one unit in length, lying on its surface. In practice there are three common methods of determining this property, namely, (a) the rise of the liquid in a capillary tube, (b) the size of a drop falling from an annular orifice, and (c) the pull required to detach a circular ring of wire from the liquid surface.

The most accurate method for determining the surface tension of a liquid consists in measuring the height to which it rises in a capillary tube. The surface tension can be calculated from the density of the solution and the height to which it rises in a previously calibrated tube. This method is not so conveniently applied to industrial plating baths as the two methods described below.

A simple and convenient procedure to use is the drop-weight method, in which the surface tension is measured by the size of the drop that falls from an annular orifice. The solution is drawn into a glass tube having a capillary with the lower tip ground flat. The tube is marked for a definite volume to be used and is called a stalagmometer. The number of drops of pure water is compared with the number of drops of the plating bath to the measured volume at the same temperature.

The detached-ring method is usually applied by means of a tensiometer. An accurately constructed platinum-iridium ring is withdrawn from the surface of the solution to be measured by slowly applying tension to a wire connected to the ring. The amount of pull is indicated upon a circular graduated scale which is calibrated to give readings in dynes of force. Calibration is done by measuring the surface tension of water at the same temperature. The measurement of

surface tension can be used only to establish a minimum concentration of wetting agent necessary for a given drop in surface tension.

CONDUCTIVITY MEASUREMENTS

Since most of the plating baths are highly conductive solutions, it is important that the conductivity be known for maximum operating efficiency. For example, most alkaline cleaners operating at line voltage derive their cleaning power from the high conductivity of the solutions, their high pH, and elevated operating temperatures which permit the evolution of copious amounts of gas. Therefore, it is of practical importance to measure and control the conductivity of the cleaner solution. The cleaner composition limits are usually quite broad, so that it is possible to operate for varying lengths of time, before actual chemical analysis is required, by conductivity control alone utilizing an operating graph. The cleaner may be held within conductivity limits equivalent to those giving good cleaning action for a freshly prepared cleaner by the addition of cleaner compound or the most important constituent, sodium hydroxide. Control by conductivity measurements alone should not be carried out for too long a period of time; depending on operating conditions, one week may be the limit, since factors such as carbonate buildup will eventually upset conductivity as a measure of cleaning power. The same technique may be used to determine the acid concentration in pickling baths, contamination of rinse tanks, and conductivity of plating solutions.

The determination of conductivity resolves itself into measuring the resistance with an industrial adaptation of the Wheatstone bridge. In industrial applications where a tolerance in the order of 1% is permissible, ordinary 60-cycle alternating current from the lighting or power circuit may be used provided that the electrodes are approximately the size of the standard cell, i.e., 1 cm apart and 1 sq cm in cross section. Alternating rather than direct current is used to overcome polarization errors occurring at the electrodes.

The dip or conductivity cell electrodes can usually be constructed of nickel surrounded by an insulating material such as hard rubber. It is not necessary to know the area of electrodes or the distance between them, since a cell constant can be readily determined. The resistance of the cell is measured when it contains a solution of known specific conductance. One of the solutions used for this purpose is 0.02 M solution of potassium chloride. The reciprocal of resistance is equivalent to the conductivity.

For 0.02 *M* potassium chloride at 25°C,

$$K = 0.002768R$$

where *K* is the cell constant converting measured conductivity to specific conductivity. The specific conductivity of any solution is then obtained directly by dividing the constant by the measured resistance.*

HYDROMETER MEASUREMENTS

Perhaps the simplest test that can be applied to the acid pickle, alkaline cleaner, and plating solutions is the measurement of specific gravity with a hydrometer. These measurements are rapid and can be taken directly at the tank with the proper corrections. They can indicate whether the solution under test is within overall concentration limits, whether stratification or incomplete mixing has occurred, whether decomposition products are building up too rapidly, etc. The hydrometer is commonly used to control the acid concentrations in pickling, chromic acid concentrations in chromium plating solutions, and copper sulfate concentrations in copper plating baths. However, the hydrometer can be conveniently extended to cover other types of more complex baths, if the operating limits are not too narrow, but care should be taken against its indiscriminate use when it is not a proper guide to the concentration of active constituents of the solutions.

POLAROGRAPHIC MEASUREMENTS

The value of polarographic analysis is beginning to be appreciated by the electrochemical industry as a rapid means of analysis for plating solutions. Although considerable developmental work is needed on both the instrument and technique before the method will be a common laboratory procedure, the polarograph may well prove to be an instrument which will give the electroplater analytical data within minutes instead of hours.

As the polarographic method is a modification of the dropping mercury cathode,^{9,10} both current and emf are measured. The method differs from the common potentiometric methods in that the electrolysis is carried out with very small electrodes for short periods of time and is concerned only with the electrode solution interface (a thin film of solution in direct contact with the electrode). Therefore, in-

* Reference 4, p. 401.

stead of changing the composition of the main body of the solution 5 to 10 ml, only the ratio of oxidant to reductant present at the interface is changed.

The electrical circuit consists essentially of a source and a means of providing a known variable emf to the electrolysis cell and a device for measuring the resulting current against applied voltage, usually less than 5×10^{-5} amp. A plot of observed current against applied voltage gives a typical polarogram. The cathode is a small stream of mercury falling in drops from a capillary tube with a fairly large pool of mercury as the anode in the bottom of the vessel. If the current is kept very low (10^{-6} amp) on this large anode area, the potential remains constant and variations in the emf of the cell are due to changes in the cathode potential. However, current can be measured by applying cemf between the mercury electrodes. When the potential is increased slowly, a corresponding change in the current is recorded. The discharge of an ion or the occurrence of any new process at the cathode is indicated by a sudden rise in current with only minor changes in emf.

CONTROL OF THE DEPOSIT

HYDROGEN EMBRITTLEMENT

The basis metal adsorbs nascent hydrogen during the pickling operation, whether it be cathodic or soak pickling, and during the plating operation some of the hydrogen liberated at the cathode is adsorbed, either by the basis metal or by occlusion into the plate. This action results in lowering the ductility of the basis metal and in some cases increases porosity, and the plate will also exhibit poor adherence. In general, anodic cleaning and pickling should be used whenever possible to minimize the effects of hydrogen embrittlement. Hydrogen retained in the coating itself after plating has two directions available for diffusion: (a) effusion into the atmosphere, and (b) infusion into the basis metal. Under the phenomenal conditions of partial pressure obtained in these systems, diffusion into the basis metal can be as likely as effusion into the atmosphere. An appreciable proportion of the inner layers of the coating can be expected to eject their hydrogen into the basis metal after plating just as effectively as during the plating or pickling operation itself.

In general, hydrogen embrittlement should be minimized in the plating cycle wherever possible. It can be relieved by heat treatment

appropriate to the basis metal and plate, i.e., at the maximum temperature and under conditions which will injure neither.

TENSILE STRENGTH

Tensile strength is a measure of the force required to pull the metal apart and is expressed as the maximum load divided by the initial cross-sectional area of the specimen. This property of electrodeposits is an important indication of the amount of distortion the plate will withstand before it will fracture.

The successful measurement of tensile strength requires rigid standardization of procedure in the preparation of samples and performance of the test. The standard forms used are tubes or flat sheets with reduced sections. The strips can be prepared by plating on stainless steel and pulling off the deposit which is then cut to size. Sheets or tubes may be plated on copper and the copper dissolved with nitric or chromic-sulfuric acid mixture if the deposit is unaffected by these acids. An alternative method is to plate 0.0001 to 0.0005 in. of a low-melting metal on a rod, and then plate the metal to be tested over this intermediate layer. On heating to the melting point of the intermediate layer, the rod may be pushed out, leaving a tube of the metal to be tested. For thin specimens, a standard tensile testing machine used by the paper industry is very appropriate.

After the samples are electroformed, they are cut to the size specified by A.S.T.M. Designation E8-46 and pulled in any of the usual tensile machines. The rate of application of the load should be carefully controlled, preferably according to A.S.T.M. standards.¹¹ The maximum load required to break the specimen is divided by the initial cross-sectional area tested to give the tensile strength in pounds per square inch.

DUCTILITY

Ductility in a deposit is of prime importance in case the plate is subjected to occasional or periodic deformation or to forming or machining operations. Qualitatively, ductility of a deposit is judged by means of the "fingernail test," which is made on a section of the metal 0.001 in. thick deposited on and stripped from stainless steel. If a crease in the foil can be opened without fracturing, the metal is considered ductile. This method is commonly used to judge the ductility of nickel deposits.

The property most frequently associated with ductility is elonga-

tion. This is determined by running the tensile test described in connection with tensile strength. The elongation of the specimen when stretched to fracture is measured and is expressed as per cent elongation in a specified gage length. Tests for elongation are affected appreciably by the thickness of the specimen. Rochl¹² found that, if the deposit to be tested is at least 0.03 in. thick, the ductility is independent of the thickness.

Another possible method for measuring the comparative ductility of an electrodeposited metal is the Modified Erickson Cup Test. This method involves plating on a flat strip of basis metal and elongating a small section of the test specimen by transmitting a load to the flat section by a hardened steel sphere. This test is carried out by the Tinius Olsen Ductility Machine, which operates by slowly pressing a steel ball against the test piece. The load in pounds and the deflection in inches are recorded on two gages.

STRESS

Internal stress in electrodeposited metals may have a profound effect on the quality of the plate. Such residual stress may be affected by temperature, pH, current density, addition agents, or impurities in the bath. The result may be either tensile or compressive stress, which will affect the adhesion, continuity, or corrosion characteristics of the deposit. Most of the studies in recent years have been made on the significance and effect of stress in electrodeposited nickel.

The generally recognized methods of measuring stress in an electrodeposit consist in plating one side of a flat metal strip of known elastic modulus and measuring the curvature of the plated strip. The metal strip is held rigidly in a suitable fixture so that neither contraction nor bending can occur during plating. The plated strip is then released and allowed to assume its equilibrium curvature. The radius of the curvature of the bent strip is then determined by measuring the camber (sagitta of the arc) with a special gage or a microscope with a calibrating vernier focusing adjustment. This is the method used by Soderberg and Graham¹³ and Phillips and Clifton,¹⁴ who developed suitable formulas for stress calculations. Another method, developed at the Bureau of Standards and reported by Brenner and Senderoff,¹⁵ uses a spiral metal strip instead of a flat strip. Designated as the spiral contractometer, this instrument measures displacement caused by stress in the deposit during plating, the results being read directly on the dial of the instrument.

HULL CELL

The most generally used empirical plating range cell, the Hull cell,^{16, 17} serves many purposes in the control of plating baths. Since it covers a wide current density range above and below that used in normal operation, many plating bath difficulties can be predicted before the effect is seen in production. Typical factors that may be controlled by the Hull cell test are: addition agents, decomposition products, bath impurities, *pH*, and bath composition. Each type of plating

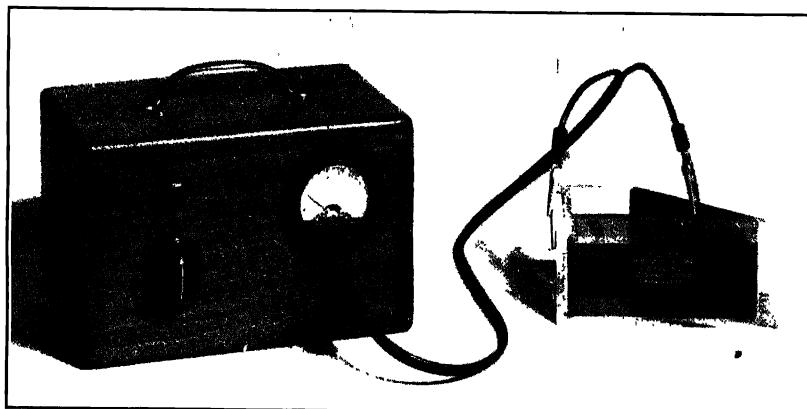


Fig. 1. Hull cell. (Courtesy R. O. Hull & Co.)

bath will show different characteristics which should be studied by the operator for proper control. In any practical case, it is advisable to run standard plates for all the important bath variables in order to become familiar with the typical appearance of a plate. Such a set of standard plates will serve as control references.

In the Hull cell test, a wide current density range is obtained by the geometric arrangement of the cathode. The current density at any point on the cathode can be estimated by the equation

$$A = C(27.7 - 48.7 \log L)$$

where A is the current density, C the total current, and L the distance along the cathode. The total current used depends on the type of bath being tested.

The preferred cell has a volume of 267 ml of solution. When making additions to this volume, 2 g are equivalent to 1 oz/gal. An anode of the metal to be plated is placed at the square end of the cell to fill the cross section. When necessary to avoid excessive polarization, a

corrugated or wire gauze anode is desirable. A $2\frac{1}{2}$ by 4 in. cathode is placed at the opposite, inclined end of the cell. The plating time and current used depend on the type of plating bath being tested. If trouble is suspected after a previously set standard test is run on the bath as it is operating, corrections should be made on a small portion of the bath and a second test should be run. When the desired results are obtained, correct additions can be made to the large bath. If the bath is agitated in actual practice, mild agitation with a stirring rod should be used during the test.

THE BENT CATHODE TEST¹⁸

This is another simple, rapid plating test which may be conveniently carried out in the vicinity of the plating tank. It is invaluable in indicating whether the bath is operating at peak efficiency, whether impurities are accumulating in the bath, and various other difficulties contributing to poor plating. Basically, this covers the normal plating range plus both higher and lower current ranges in one operation. Proper interpretation of the test plates from these procedures gives a very good indication of the operating condition of the bath itself. The apparatus commonly used consists of a 250-ml cell or beaker in a constant temperature bath with an anode approximately $\frac{1}{8}$ in. thick and 1.5 in. wide, and a length sufficient to extend through the depth of the bath. The anode is situated directly opposite the cathode and is placed flat against the side of the container. The cathode is usually prepared from light gage copper and presents a plating surface 1 in. wide and 2.5 in. long. It is bent at right angles 1 in. from the bottom, and the bent section protrudes toward the anode. The actual depth of the cathode into the plating solution is 1.5 in. The geometry of the cathode presents ideally recessed and protruding sections and is an excellent specimen for throwing power studies. The apparatus is completed by connecting an ammeter and a rheostat to the cathode line and connecting a voltmeter to both electrodes.

The appearance and character of the deposit on the protruded portion in the radii and vertical section of the bent cathode exhibit to the experienced observer considerable information on the plating conditions of the bath.

BEND TESTS FOR ADHESION

The qualitative tests can be classed as bend tests^{19, 20} and blister tests.²¹ The bend tests comprise bending or flexing of the plated

object in such a manner as the specimen will permit. The bending is frequently reversed and repeated until the basis metal is fractured. Any evidence of peeling, chipping, or flaking of the deposit is taken as cause for rejection.

In most cases the qualitative test is made by hand, the test piece being held firmly by pliers or vise and bent as sharply as possible. However, special setups have been devised which more or less give a quantitative bend test so as to permit some degree of standardization and reproducibility.

THE CONICAL MANDREL TEST

In this test a finished panel is wrapped around a conical mandrel. The applied force elongates the coating from 2.2 to 28% on these special panels. At the same time the specimen is given a bend of varying radius, and comparison is made between the maximum radii for cracking or flaking of the coating.

TWIST OR ROCKING TEST

In this test the specimen is bent into a V shape and is then given repeated bends back and forth in a direction perpendicular to the plane of the V. This rolling twist occurs in the vicinity of the V.

DEFORMATION TEST

This test consists in bending the specimen through 720° in 180° stages. Observations at each stage give an indication not only of the degree of adhesion but also of the ductility of the coating. Absence of separation of the coating from the basis metal at 720° constitutes satisfactory adhesion.

ANNEALING TESTS FOR ADHESION

Experience has shown that difference between coefficients of expansion of the plate and basis metal can be conveniently used as an adhesion check for the plate, especially when the differences are large. This difference, on heating, results in a severe straining at the interface which produces cracks, blisters, or peeling when the plate adhesion is weak.

The heating tests have the advantage of not damaging the test piece, as they yield an acceptable product if the adhesion is satisfactory, and they may be used for items for which the bend test is not applicable. They also have the advantage of rapidly exposing failures, as sometimes a particular plated article might not blister for weeks

under normal exposure conditions, whereas the same result might be obtained in one hour at an elevated temperature.

The heating tests may sometimes be misleading, as in numerous cases the bond strength is improved by the annealing treatment. In such instances it is well to subject the entire production to this treatment. This increase in bond strength is usually due either to diffusion of the coating into the basis metal or to the elimination of hydrogen at or near the interface. Sometimes the diffusion layer increases brittleness, and the plate fractures or peels readily. Under any conditions, the temperature used for the heating test will depend upon the properties of the plated metals being evaluated, and their tendency to react with basis metals. Where there is an oxidation tendency, it may be necessary to use a reducing atmosphere.

Alloy Plating

CHARLES L. FAUST *

Alloy deposition in practice and in research shows distinctive benefits and features not attainable by electrodeposition of single metals. In general, one can expect alloy plates to be denser and harder than plates of the single metals involved. In certain composition ranges, alloy plates have been found more corrosion resistant; more protective for the basis metal; brighter than either single metal plate; more readily buffed; tougher and stronger; more suitable for subsequent plates and chemical treatments; and deposited satisfactorily over a wider range of operating conditions than one or both of the individual metals can be. For several metals, current efficiency has been improved, and actual deposition of a metal such as tungsten (wolfram), or germanium, not platable pure, or deposition of nickel and iron from cyanides has been attained by codeposition.

The practical importance of bright plating is well recognized in decorative finishing, and alloy plates have an important position. The following are established: Ni-Co;¹ Ni-Zn (or Ni-Co);^{2,3} Zn-Mo;⁴ and Cu-Zn-Sn.⁵ Tarnish-resistant properties are desirable and are realized with Cu-Zn-Sn and with "speculum" plate, Cu-Sn,⁶⁻⁸ which is the non-noble metal alloy most closely approaching silver in color. Bright speculum plate has been achieved.⁹ Red bronzes are produced, and soluble alloy anodes are used for both speculum and the red bronze. Silver is said to be made tarnish resistant by codeposition with uranium¹⁰ and bright by codeposition with antimony,¹¹ titanium, or selenium.¹² Ni-Mo is deposited for a lustrous, black finish.¹³ The extensive use of brass electroplate is well known, and the process is described in Chapter 4. Ni-Co alloy is disclosed as having advantages for finishing magnesium alloys.¹⁴ True bronzes (90% Cu-10% Sn composition level) are suggested for decorative finishes,¹⁵ and the "smoothing action" of codepositing a small amount of a second metal

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with nickel has been described.¹⁶ Bright Sn-Ni alloy plate is among the most recent accomplishments.¹⁷

For protection of other metals, the porosity, the relative electrode potential for galvanic protection, and the nature of the corrosion products of the deposited metal are important. Sn-Zn¹⁸ alloy plate has interesting prospects for benefits in all three of those properties.^{19, 20} Enough zinc is in the alloy to make the potential less noble relative to that of steel and yet retain many of the characteristics of tin and offer galvanic protection under many conditions. Similar effects for corrosion protection can be obtained by other combinations of metals in alloy plates. In a specialized form of protection, Pb-Sn alloy deposited on anodes constructed of other metals renders them insoluble in chromic acid plating baths. The method of deposition has been described.²¹ The variability of corrosion conditions renders impossible any specific designation of alloy plates having wide utility in protective value. Nevertheless, the possibilities for alloy plates are interesting, with particular reference to Cd-Zn,^{22, 25} Cu-Sn,^{26, 27} W-Ni,²⁸ W-Co, W-Ni,²⁹ and tungsten alloys;³⁰ W-Ni, W-Co, W-Fe,³¹ Sn-Ni,¹⁷ and lead alloys with thallium,³² bismuth,³³ and silver.^{31, 35}

Important applications for alloy plates will be found in high-temperature service. Composite parts will consist of the basis metal and an alloy-electroplated surface. The basis is selected for its ease in fabrication and mechanical properties at the high temperature. The plated alloy is selected for its chemical and physical resistance under the conditions of service. Most of the alloys having high temperature resistance to oxidation or other forms of surface chemical attack are difficult to fabricate. The deposition of the alloys has been started with the work on W-Co, W-Ni,^{28, 29} and tungsten alloys;³⁰ W-Co, W-Ni, W-Fe,³¹ and with researches underway on chromium and molybdenum alloys.

The last comments in the preceding paragraph refer to protective finishing against high temperature corrosion, but can become so important to performance as to be included with "engineering plating." In this field, alloy plating has achieved commercial success, and it has a promising future, because there are significant metallurgical possibilities. For the lining of bearings by alloy plating:³⁶ (1) thinner liners can be produced, requiring very little, if any, machining after deposition, so scrap is greatly reduced and production is facilitated; (2) the liner is applied in a "cold casting" process that does not subject the backing material to heat treatment or tempering; (3) alloys can be made of metals difficult to alloy in any other way;^{37, 38} and (4)

liners having unusually fine grain size and structural uniformity are produced. Pure silver electroplate, when overlaid with successive layers of lead and indium or Pb-Sn alloy plate, give outstanding performance as a bearing liner for such heavy duty, internal combustion engines as those used in airplanes, tanks, and diesel engines, particularly during World War II.

The indium plate prevents hot oil erosion of the lead plate which imparts "oiliness" to the silver plate bearing; whereas the Pb-Sn alloy (approx. 5 to 10% Sn, remainder Pb) performed both functions. Ag-Pb³⁴ alloy plate functions as well as a bearing without the need for an overlay to provide the other features, as does the two- and three-layer composite.

Cu-graphite,³⁵ Sn-graphite,* Ag-Cd,³⁶ and Cu-Pb⁴⁰ alloys have been electrodeposited in bearing studies. Cu-Pb electrodeposited bearing liners show the same load-carrying capacity as bearings poured in the usual way.⁴¹ Pb-Sb-Sn alloys are deposited for bearings.^{42, 43}

Corrosion resistance and improved "wear" performance are disclosed for silver with which thallium is codeposited for a bearing alloy.⁴⁴ Sensitive, high temperature thermopiles,⁴⁵ iron alloys having exceptional magnetic properties,⁴⁶ alloys for electroforming thin sheets,⁴⁷ and alloy materials that can be electrodeposited for building up worn parts or for special surfacing have been proposed. Cu-Zn alloy plating to exact composition has been a large scale commercial process for years to provide a bonding layer for rubber coating steel, aluminum, and other metals.⁴⁸ For securing rubber adhesion, tungsten alloys are also disclosed.⁴⁹ The applications of Ag-Cu and Ni-Fe alloy plates are disclosed as undercoats for enamel.⁵⁰ Intermediate alloy layers are deposited to improve subsequent nickel and chromium plate.⁵¹⁻⁵⁵ Pb-Sn solders have been refined and manufactured for many years by electrodeposition of the alloy.^{56, 57}

The question might be raised, "Are codeposited metals alloys?". The answer is, "They are." They usually have a phase structure comparable with that indicated as stable for the temperature at which the electrodeposited alloy was formed. Furthermore, the metallurgical nature of alloy electroplates is of interest to any user of them.

X-ray examination reveals that, apart from the superstructure of β -brass, the same phases occur in alloys deposited electrolytically as in melt-formed alloys.⁵⁸ Phase limits closely agree. Debye-Scherrer

* Reference 27, p. 16.

interference rings show a strong distortion of the lattice, particularly in the α -phase. Electrodeposited α -brass is harder than the cast form, but hardness of the β -, γ -, and ϵ -phases is unaffected. Resistivities of the alloy plates are normal, and hydrogen overvoltage on ϵ - and η -alloy plates is the same as for pure zinc, but for copper-rich alloy plates, hydrogen overvoltage is lower.

Electrodeposited Ag-Cd alloys containing 96-31% Cd were shown by x-ray analysis to be either solid solutions or compounds.^{59, 60} In the region of the β -phase (44-57% Ag) another phase was seen, the β' -phase, having a hexagonal lattice, stable at low temperatures.

In electrodeposited Ag-Zn alloys, all phases are present according to the phase diagram except the ζ -phase.⁶¹ Except for the ζ -phase, all correspond in composition to those of the thermally prepared alloys. The α -phase is the same structure as in cast alloys. The β -phase, body-centered cubic, is identical with that in alloys of the same composition cast and quenched from temperatures above the transformation, $\beta \rightleftharpoons \zeta$.

X-ray study of Fe-Ni alloy electroplates resulted in agreement with thermally prepared alloys.⁶² Unlike cast alloys of Ag-Pb, which have large silver crystals with lead present in the grain boundaries as dendrites, the electrodeposited Ag-Pb alloy is exceedingly fine-grained and shows no segregation of lead visible in optical microscopes. X-ray studies reveal that the silver lattice is expanded.⁶³ The electrodeposited alloy can be recrystallized without further modification and retain the fine structure.

Bright speculum plate is looked on as a unique form of the ϵ -phase Cu₆Sn₅, with abnormally expanded lattice parameters and modified composition.¹⁷ Brightness requires small crystal size and preferred orientation. Composition approaches Cu₃Sn. Irregular articles are said to be unplateable with uniform brightness, because of impossibility in practice of controlling plate composition. Rooksby¹⁷ shows that true brightness results over only a narrow composition range. This effect is a limitation of the method used, since bright speculum is now plateable, under the trade name Lustralite, uniformly on irregular parts.*

Another unusual combination of metals has succumbed to alloy deposition, Sn-Ni, a bright plate.¹⁷ The plate is a metastable, single-phase alloy similar to hexagonal Ni₃Sn₂, yet the composition is Ni₃Sn. Cast 65% Sn-35% Ni is a mixture of γ and γ dash, Ni₃Sn₂ + Ni₃Sn₄.

* Process of the City Auto Stamping Company

At 400°C the alloy plate decomposes to normal $\text{Ni}_3\text{Sn}_2 + \text{Ni}_3\text{Sn}_4$. The Sn-Ni alloy is comparable with speculum (Cu-Sn) plate. Both alloy plates are more dull when random oriented. The bright Sn-Ni plate on copper is oriented with (110) planes parallel to the basis metal surface.

From the x-ray investigations of electrodeposited alloys, the conclusion can be reached that they are alloys in every sense of the word. When the proper metal combination is used, they are subject to hardening by heat treating, which causes solid precipitation.²⁹

An interesting and important aspect of alloys obtained by plating is the forming of them by heat treating after deposition of different metals in individual layers. Since this is not actually "alloy deposition," reference is made here only to the extensive bibliography⁶ and the historical review of the subject.⁶¹

This brief introduction cannot adequately disclose the scope of alloy plating work, but it will indicate to the reader the important role that alloy plating can assume. More extensive reviews are reported elsewhere.³⁶ There are enough publications to show the general procedure to be followed in securing alloy plates. The cathode and anode process control have been studied for numerous systems.

PRINCIPLES

The same principles apply to, and the same few variables control, both alloy and single-metal plating. In order to codeposit two or more metals, the variables must be combined in a way that causes the metals to codeposit at the same potential. The deposition potential of a metal or alloy is determined by the activities of cations and anions in the cathode "film" and by the temperature. The activities are functions of the ion concentrations which, in the cathode film, are determined by the rate of deposition, by the ion concentration in the bath, and by the rates of diffusion of the ions involved. Thus, there is a different "table" of deposition (and of static equilibrium) potentials for the metals, depending on the chemical nature of the electrolytic solution. There is no single, fixed set of values for static and deposition potentials of metals that is universal for all conditions. This situation makes codeposition of metals not only possible but practicable.

The deposition potentials discussed in the following paragraphs are those measured in the particular solutions of interest, or under investigation.

In an alloy plating bath, the single-electrode potentials, E^s , of the metals, as given by Eq. (1), are generally fairly close together:

$$(1) \quad E^s = E^0 + \frac{RT}{vF} \ln a^{v+}$$

The equation refers to a condition of reversible equilibrium. Since deposition usually occurs in an irreversible process, Eq. (1) cannot indicate the deposition potential which is a dynamic value associated with the discharge of cations at a definite rate in an irreversible process.

The deposition potential, E^d , as given by the equation

$$(2) \quad E^d = E^0 + \frac{RT}{vF} \ln a^{v+} - P$$

includes a term P , which exceeds $(E^d - E^s)$. In both Eqs. (1) and (2) the factor a^{v+} is the activity of the depositing cation in the film of plating bath at the cathode face. E^0 is the "standard" equilibrium electrode potential; P can be called a rate factor expressed as the extra potential required to keep the deposition going at the given speed. Calculation of a metal deposition potential by Eq. (2) requires a knowledge of the values of a^{v+} and P for the given plating conditions, i.e., current density, temperature, concentration and valence of all ions, ion mobility, pH.

The E^0 values for copper and zinc are far apart in the standard emf series, and codeposition prospects would appear to be remote. This difference in potential can be eliminated or even reversed by changing the values of a^{v+} , as would result from a large change in concentration of the ions of the depositing metals, such as by complex ion formation. Calculations, for illustration, show that the copper ion concentration can be made much smaller than the zinc ion concentration in cyanide solutions as used for Zn-Cu alloy plating.⁶⁵ In a solution containing simple salts of zinc and copper, the ion concentrations and the activity coefficients of the two metals are so close together that the large difference between E^0 for copper and E^0 for zinc cannot be reduced enough to permit good alloy plating. In a solution of the complex cyanide, the Cu^+ concentration can be reduced to the order of 10^{-18} moles/l, and the ion concentration ratio of $\text{Zn}^{1+}/\text{Cu}^+$ will be very large. The calculation which shows this is of general use in considerations of alloy plating solutions in which data on the molecular composition and the ionization constant of complex ions are em-

ploied. For illustration: the copper cyanide complex is taken to be $\text{Cu}(\text{CN})_3^-$, for which the ionization constant is 5.6×10^{-28} ; and the zinc cyanide complex is taken as $\text{Zn}(\text{CN})_4^{=}$, for which the ionization constant is 1.3×10^{-17} . Then

$$(3) \quad \frac{(\text{Cu}^+)(\text{CN}^-)^3}{[\text{Cu}(\text{CN})_3^-]} = 5.6 \times 10^{-28}$$

$$(4) \quad \frac{(\text{Zn}^{++})(\text{CN}^-)^4}{[\text{Zn}(\text{CN})_4^=]} = 1.3 \times 10^{-17}$$

To simplify, the following abbreviations are used:

$$(\text{C}^-) = [\text{Cu}(\text{CN})_3^-] \quad \text{and} \quad (\text{Z}^=) = [\text{Zn}(\text{CN})_4^=]$$

When equilibrium is reached in a solution containing $\text{K}_2\text{Cu}(\text{CN})_3$ and $\text{K}_2\text{Zn}(\text{CN})_4$, the concentration of CN^- ions must be the same in each of the expressions (3) and (4). Thus

$$\sqrt[3]{\frac{(5.6 \times 10^{-28})(\text{C}^-)}{(\text{Cu}^+)}} = \sqrt[4]{\frac{(1.3 \times 10^{-17})(\text{Z}^=)}{(\text{Zn}^{++})}}$$

from which

$$\frac{[(\text{Zn}^{++})]^{\frac{1}{4}}}{(\text{Cu}^+)} = \frac{[(1.3 \times 10^{-17})(\text{Z}^=)]^{\frac{1}{4}}}{(5.6 \times 10^{-28})(\text{C}^-)}$$

Assuming, for the solutions containing both $\text{K}_2\text{Cu}(\text{CN})_3$ and $\text{K}_2\text{Zn}(\text{CN})_4$, that $(\text{C}^=) = 0.05$ and that $(\text{Z}^=) = 0.025$, which would be in keeping with the salt concentrations used, it follows that

$$(5) \quad \frac{(\text{Zn}^{++})^{\frac{1}{4}}}{(\text{Cu}^+)} = (3.87 \times 10^{14}) \left[\frac{(\text{Z}^=)^{\frac{1}{4}}}{(\text{C}^=)} \right] \\ = 4.86 \times 10^{14}$$

Thus the concentration of the zinc ion greatly exceeds the concentration of the copper ion. The actual ratio $(\text{Zn}^{++})/(\text{Cu}^+)$ would be a little less than 4.86×10^{14} , because of the term $[(\text{Zn}^{++})]^{\frac{1}{4}}$, since the concentration of Zn^{++} is less than unity. In complex ion solutions for plating, the concentrations of metal ions are usually less than 1 mole/l.

As a further consideration, one may approximate the concentration of Cu^+ ions in a solution formed by mixing together a solution 0.05 M with respect to $\text{Cu}(\text{CN})_3^-$ and a solution 0.025 M with respect to $\text{Zn}(\text{CN})_4^=$.

In Eq. (3) let $(\text{Cu}^+) = x$, and $(\text{CN}^-) = 3x$, neglecting the value of x in $\text{Cu}(\text{CN})_3^- = (0.05 - x)$. Then

$$(x)(3x)^3 = (0.05)(5.6 \times 10^{-28})$$

whence $x = 3.19 \times 10^{-8}$

Therefore $(\text{Cu}^+) = 3.19 \times 10^{-8}$

in the copper solution and

$$(\text{CN}^-) = 9.57 \times 10^{-8}$$

A similar calculation for the concentration of (Zn^{++}) and (CN^-) in the zinc solution [using Eq. (4)] gives

$$(\text{Zn}^{++}) = 6.62 \times 10^{-5}$$

$$(\text{CN}^-) = 2.65 \times 10^{-4}$$

After the two solutions are mixed, the CN^- ion concentration would be approximately that in the zinc solution, i.e., $(\text{CN}^-) = 2.65 \times 10^{-4}$, since the value in the copper solution is so much lower. Then an approximation of the copper ion concentration is again given by Eq. (3), or

$$\frac{(\text{Cu}^+)(2.65 \times 10^{-4})^3}{0.05} = 5.6 \times 10^{-28}$$

$$\therefore (\text{Cu}^+) = 1.50 \times 10^{-18}$$

From these approximate values, then,

$$\frac{(\text{Zn}^{++})}{(\text{Cu}^+)} = \frac{6.62 \times 10^{-5}}{1.50 \times 10^{-18}} = 4.39 \times 10^{13}$$

which value is of the order of that expected according to the preceding calculations.

In a manner analogous to this illustration with copper and zinc complexes, calculations can be made to determine whether complex ion formation brings the metal ion concentrations close together.

The above-calculated molar concentrations of Zn^{++} and Cu^+ can be used in Eq. (1) instead of a^{*+} for an approximation of the two equilibrium electrode potentials, respectively, for the 0.025 M $\text{Zn}(\text{CN})_4^{2-}$ solution and the 0.05 M $\text{Cu}(\text{CN})_3^{2-}$ solution. At 25°C, E° for copper in equilibrium with Cu^+ is +0.52 v, and E° for zinc in equilibrium with Zn^{++} is -0.76 v. Accordingly, at 25°C,

$$\text{for Cu: } E^\circ = 0.52 + \frac{0.0592}{1} \log 3.9 \times 10^{-8}$$

$$= 0.08 \text{ v}$$

for Zn: $E^{\circ} = -0.76 + \frac{0.0592}{2} \log 6.62 \times 10^{-5}$
 $= -0.85 \text{ v}$

Although the calculation reveals that the zinc and copper potentials have been brought nearer together, there is still a spread that might appear too great to allow codeposition. When the solutions are mixed, the Cu^{+1} concentration is 1.5×10^{-18} . Then for copper

$$E^{\circ} = 0.52 + \frac{0.0592}{1} \log 1.5 \times 10^{-18}$$
 $= -0.47 \text{ v}$

At an ion concentration of the order of 10^{-18} , the activity of that ion will be at least that small and probably smaller, so the actual value of E° for copper will be more negative than -0.47 v . Thus, owing to the effect of $\text{Zn}(\text{CN})_4^{2-}$, E° for copper approaches much closer to that of zinc in the mixed solution. From such calculations using ion concentrations, it could be reasoned that codeposition of copper and zinc is a possibility and depends upon the term P in Eq. (2) to eliminate effectually the remaining difference, so that the deposition potentials become essentially the same. This is known to be accomplished in brass deposition.

Such solutions in which the relative ion concentration of the more noble metal can be made considerably less than that of the less noble metal are good prospects for alloy plating. The calculation of probable ion concentrations can only be indicative of a prospect, because the measured concentrations are those in the body of the plating solution and not those of the ions in the cathode film. The latter is the important location, and ion concentrations there are determined by their relative diffusion rates.

In discussion of Au-Cu alloy plating, Dole⁶⁶ presents calculations to show that the gold deposition is controlled by the rate of diffusion of the gold cyanide complex ion. Copper deposition in this system is not explained by the same diffusion theory, and the copper-to-gold deposition-current ratio is smaller than would be predicted according to the diffusion rates. Whereas the proportion of the current depositing gold is controlled by diffusion of the gold complex, the copper current is thought to be controlled by the rate of dissociation of the copper cyanide complex. The relative diffusion and dissociation rates become important considerations in any alloy plating study.

Parks and LeBaron⁶⁷ have empirically developed an equation that is interesting in the study of alloy deposition. The limiting concentration of the second metal in the bath at which pure second metal will deposit is shown as a function of the valences of the two metals, the difference in single deposition potentials, the equivalent weights of the codepositing metals, and the cathode current density, where mono- and bivalent metals are involved in acid baths.

$$(6) \quad L = \frac{aZ_1^2 - bZ_2^2}{Z_2^2 + cZ_1^2} \cdot \left(\frac{1}{N} \right)^{1/2} \cdot \frac{E_L}{E_H} \cdot \log \text{c.d.}$$

Also, $L = C_1/C_2$, where C_1 is the concentration of cation of lower cathode potential at the limit of codeposition. Z_1 is the valence of ions of lower cathode potential; Z_2 is the valence of ions of higher cathode potential. N is the difference in cathode potentials of the pure metals at the given cathode current density. E_L is the equivalent weight of metal of lower cathode potential; E_H is the equivalent weight of metal of higher cathode potential. c.d. is the cathode current density (ma/sq cm). a , b , and c are constants which Parks and LeBaron empirically evaluated from data on several combinations of codepositing metals. The equation accounts for the ratio of ion activities in codeposition, since it includes the valence and concentration ratio on which activities are dependent. The effect of other variables, not included, would be to influence the term N and the constants.

These variables influence the rate at which metal ions are brought to the cathode layer and the rate at which they are removed by deposition. Inasmuch as the same variables determine the ion concentration in the cathode liquor layer, they also influence the actual value of a^{v+} . Therefore a certain type of bath can be used for alloy plating when for two metals, M_1 and M_2 , the ion relationships in the liquor layer adjacent to the cathode are such that a_1^{v+} and P_1 have values relative to a_2^{v+} and P_2 during deposition which offset the differences between E_1^0 and E_2^0 . Then, both metals will deposit at the same deposition potential, E^d . The potential of the alloy deposition must be more noble than that of both individual metals and of hydrogen from a given solution, if aqueous solutions are involved.

No way has yet been found for directly measuring a^{v+} and P for the irreversible process of metal deposition. Although Eqs. (1) and (2) can be derived by several methods, neither the method nor the equation gives any information about the nature of the process occurring in the cathode film during electrodeposition.

Fortunately, we can measure single-electrode potentials and single-metal deposition potentials under conditions where certain factors are

known. This information can be used indirectly in alloy plating studies.

Those solutions of the metal salts in which the single-electrode potentials E_1^s and E_2^s are quite close together obviously indicate that ion activities of the two metals are such as to offset differences in standard potentials. However, the single-electrode potentials merely indicate what types of solutions should be used in measuring deposition potentials. In baths where E_1^s and E_2^s are close together, E_1^d and

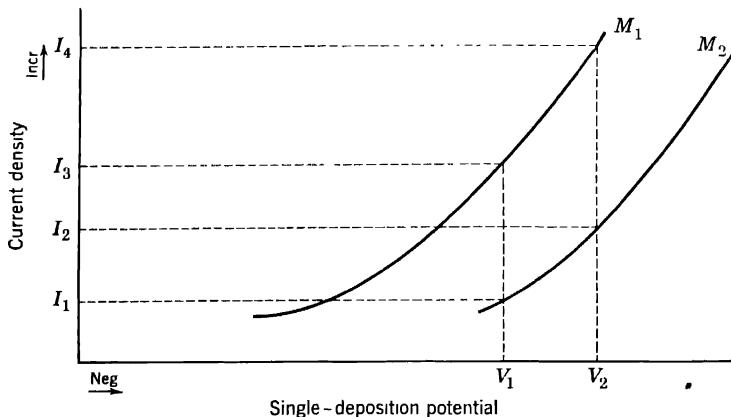


Fig. 1. Single-electrode potentials of metals M_1 and M_2 versus current density in the same type of bath.

E_2^d should be measured at several different current densities, temperatures, pH values, bath concentrations, etc. When the single-deposition potentials can be made the same, or nearly the same, for two metals when each is separately in the same type, or compatible types, of solutions when mixed, i.e., E_1^d equals E_2^d , a good prospect for an alloy plating bath is found. Figure 1 shows a representative chart depicting the change in single-deposition potentials of each of two metals M_1 and M_2 as the current density is increased. There is a range where potentials are the same for both metals. Yet, where the potentials are the same, the current densities associated with those potentials are different.

Figure 1 can be said to indicate that the bath "might" codeposit M_1 and M_2 at a deposition potential V_1 , in amounts proportional to I_3 and I_1 , and at V_2 , proportional to I_4 and I_2 . The expression "might codeposit" is used because *controlling factors* are interdependent. The M_1 and M_2 curves were determined separately, when only one metal was depositing. In this case the values for a_1^{v+} , P_1 , a_2^{v+} , and P_2 were not

influenced by the codeposition of any other cations (assuming 100% current efficiency of deposition and, therefore, no hydrogen deposition).

If M_1 and M_2 were in the same bath and the deposition potentials E_1^d and E_2^d could be measured during codeposition, the values quite

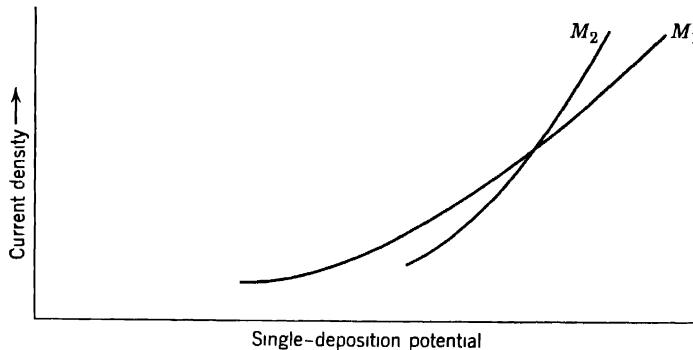


Fig. 2.

likely would not equal V_1 and V_2 for corresponding single plating conditions. When M_1 and M_2 are codepositing from the same bath under conditions thought to be the same as assumed for Fig. 1, the actual relative deposition potentials might be found to exist as shown by Fig. 2, if some way were known for determining single-deposition

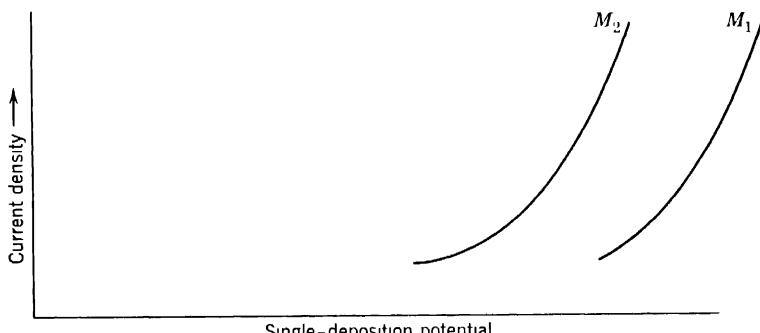


Fig. 3

potentials during codeposition. In extreme cases, depending on current densities and polarization effects, Fig. 3 would be obtained.

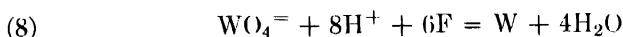
Codepositing metals "influence each other." When M_1^{v+} and M_2^{v+} are both present in the cathode film during codeposition, a_1^{v+} and a_2^{v+} are probably different respectively from the relative values when the ions of only one metal are present, as in single deposition.

Likewise, the polarization factors influencing P_1 and P_2 for each metal relative to the other and to hydrogen are likely to differ in alloy and in single-metal deposition. Therefore Eq. (2) and single-deposition potential measurements are of only indirect use in alloy plating.

Single-deposition studies might even show little or no possibility of alloy deposition with some metals in certain baths; for example, nickel and iron from cyanide or tungsten from alkaline baths, which, if tried in single deposition, would be discarded as unfavorable for alloy deposition. When these metals are in such "nonplating" baths containing other metals that can deposit out, the "unplateable" metal will codeposit under certain conditions. For example, Cu-Ni,⁶⁸ Cu-Fe,⁶⁹ Cu-Zn-Ni,⁷⁰ Cu-Ni-Fe,⁷¹ Ag-Ni,^{72,73} Au-Ni,⁷⁴ have been deposited from cyanide baths, and tungsten alloys and Re-Ni alloys⁷⁵ from alkaline solutions.^{28,76} No alloy plating prospect should be overlooked merely because one of the metals cannot be deposited singly from one or the other bath.

The comments on tungsten plating from alkaline baths and of nickel and iron from cyanide baths need further amplification. Actually, a thin film of each of these metals can be deposited, but, once coverage is completed, deposition of the metal stops and that of hydrogen continues. On the basis of metal involved, the deposition potential of tungsten (or of nickel and iron) appears to be more noble than that of hydrogen, but, as soon as a tungsten surface is presented, this relationship no longer holds, and hydrogen deposition potential is then more noble. Overvoltage of hydrogen deposition is known to be related to the kind of metal or alloy involved. These difficultly depositable metals could be considered codepositable, because the alloy plate retains a position relatively more noble than hydrogen.

A "catalytic theory" has been proposed to explain the codeposition of tungsten with such metals as iron, nickel, and cobalt.⁷⁷ The essential process involves two cathode reactions:



A thin deposit of metal, M , is formed on the cathode according to (7), then it acts as a catalyst for (8). When the cathode is covered with tungsten, reaction (8) stops and M is deposited again, and so on. Metal deposition on a cathode through the action of H^+ also explains the deposition of chromium from chromic acid (CrO_3) solutions.⁷⁸ This reduction process is worthy of further study in connection with the

electrodeposition of other metals. These remarks, of course, refer to aqueous solutions and to nonaqueous solutions containing compounds ionizable to produce electrodedepositable hydrogen.

Electrochemically considered, metal deposition frequently involves "alloy plating in which hydrogen is the codepositing element," even when hydrogen is finally discharged as a gas, since the codeposition conditions are fulfilled. Alloy plating, referring to metals, merely changes this prospect to "hydrogen and two or more metals."

The previously used expression "might codeposit" in reference to two or more metals is too broad from a practical point of view. It should be narrowed down to "might codeposit in acceptable form." Thus Figs. 1 and 2 show possible codeposition potentials, but these bear no relation per se to physical form of the plate. One frequently finds that at V_2 , for example, or even at V_1 , the limiting current density for sound plate of M_1 has been exceeded, although the limiting current density for alloy plate has not been. Codeposition frequently has no practical value, unless addition agents can be used to improve the physical condition of the plate. Examples are found in Ag-Pb, Ni-Zn, Cu-Pb, and Cu-Sn plating. On the other hand, instances of the reverse are true; that is, acceptable plates are produced beyond the current density limits indicated in Figs. 1 and 2. In this case, codeposition has raised the apparent limiting current density of one of the two metals. Examples are found in plating of Cd-Ag, bright Ni-Zn, Cu-Sn, and Ag-Pb alloys.

When problems of the physical condition of the plate arise, the alloy plater can turn to "tricks" known to all platers, such as use of addition agents, altering the pH, changing the degree of agitation, varying the bath temperature. These are some of the reasons why each alloy plating problem is finally solved only by direct experiment. The optimum combination of the several variables and operation ranges are "tailor made" for each particular alloy.

By careful study of the many references in the literature bearing directly on a given metal combination or on other combinations containing one of the metals, probable alloy plating baths can frequently be determined in a few experiments. Tedious measurements of deposition potential are then eliminated. In any case, the optimum bath composition must be developed empirically.

Many microscopic examinations of sections of alloy deposits have revealed a layer structure apparently consisting of two different compositions.^{79, 81} The layer effects could result from periodic changes in deposition potential. The periodicity would be caused by rela-

tively more rapid depletion of more noble metal ions in the cathode film. As the more noble ions are depleted, the less noble ions increase in concentration or activity, so they plate out in larger amounts, until their concentration is in turn depleted. Consequently, a periodic alteration in deposition ratio might occur which would give rise to banding in the plate. The bands vary in number and thickness according to the relative ion activities, individual overvoltages, pH effects, and addition agent effect.

All experimental development should be made with as complete freedom from bath impurities as possible. Frequently, alloy deposition baths have been discarded in preliminary work because of poor plates. The actual cause of the poor plates was the small amounts of other metals or organic matter in the bath. After the pure solution experiments have led to a bath and reproducible operating conditions, the tolerance for impurities should be studied.

After the conditions for codeposition have been found, only the first step toward a commercial process is completed. Next, the anode reactions and the effect on them of variation in the several factors must be studied.

THE ANODES IN ALLOY DEPOSITION

The anode process in alloy deposition is equally as important as the cathode process. Frequently a bath that proves suitable for deposition of a given alloy is entirely unsuitable for use with soluble anodes. Therefore the anode process should be studied as soon as any bath shows promise of producing the desired alloy plate. The anodes can be either (1) soluble alloys; (2) soluble, separate anodes of each metal; (3) insoluble, with metal makeup by addition of suitable compounds of the metals; or (4) combinations of (1), (2), and (3).

Alloy anodes provide the simplest control. Certain factors, such as phasial, physical, and chemical composition and impurities, must be taken into account.⁷⁹ Figure 4 shows the manner in which static electrode potentials depend on the composition of a binary alloy.⁸² Whenever two phases are present in an alloy anode, the possibility of selective dissolution exists. A single-phase, solid-solution-type alloy anode is normally expected to be most satisfactory. The mechanical mixtures and the alloys consisting principally of intermetallic compounds present special problems. Each of these alloy types has been used successfully as soluble anodes. When alloy anodes are unsuitable, separate anodes of each metal should be considered.

As for deposition potentials, anode dissolution potentials are not directly predicted from a simple study of static electrode potentials. Actual dissolution studies must be made in order to develop the control process. Obviously, the anodes must supply the bath with the

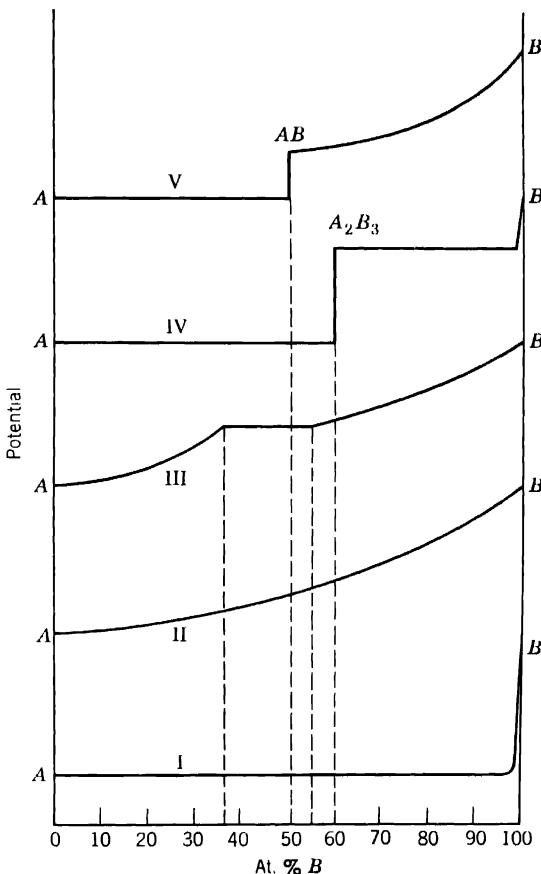


Fig. 4. Electrode potential of various types of alloys. (From Reference 82.)

codepositing metals at the same rate (or slightly greater rate to offset drag-out) and in the same ratio as codeposited.

The rate and nature of the alloy anode dissolution depend on its chemical and physical composition, the current density, temperature, type of electrolyte used, pH, agitation, etc., in a process the reverse of deposition.

Faust, Henry, and France⁷⁹ investigated control of alloy plating baths by using alloy anodes representing both single-phase homoge-

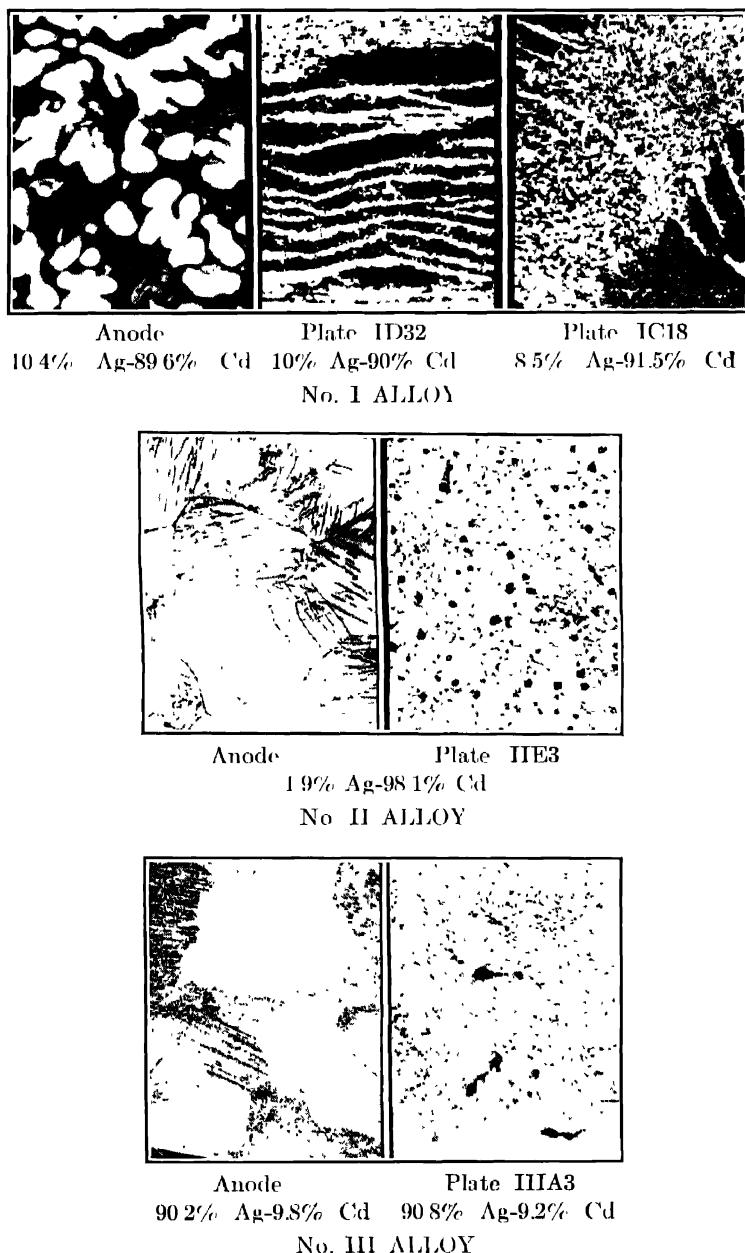


Fig. 5. Structure of Ag-Cd alloy anodes and plates.

neous and duplex structures in the Cd-Ag system. Figure 5 shows the metallographic structure of some of these anodes and the corresponding plates.

Anodes of duplex structure require closer current density control than single-phase, solid-solution-type alloys. For example, in cyanide solutions, high Cd-low Ag alloy anodes obtain a coating of silver by

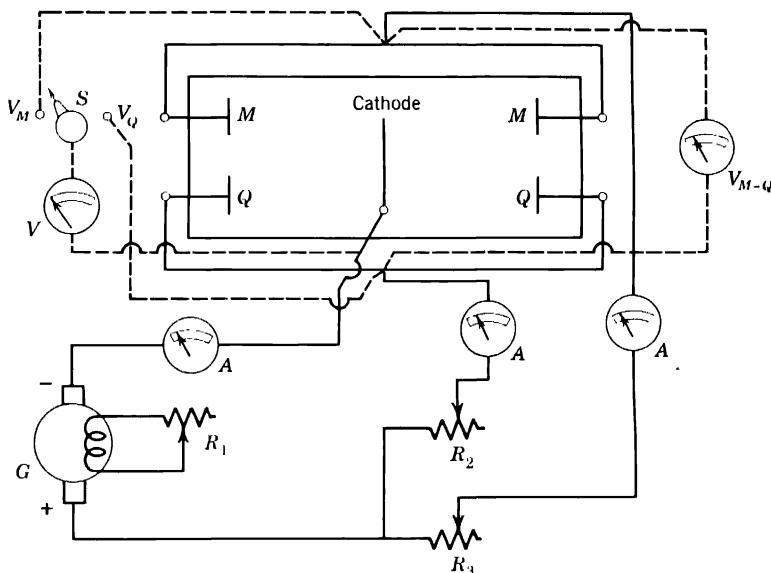


Fig. 6 Wiring diagram of plating tank using separate anode circuits for anodes of different metals, for plating a binary alloy of the metals represented as M and Q . A = ammeter; V = voltmeter; G = generator; R = resistance; S = switch; C = cathode; M and Q = anodes.

chemical displacement, and the ϵ -phase will be insoluble as an adherent coating mixed with the silver if too low anode current density is used. On the other hand, the homogeneous, solid-solution-alloy anode dissolves completely at 100% efficiency, even though silver is displaced on it. Such chemical displacement upsets the primary ion ratio for alloy composition control at the cathode.

Whenever there is a wide difference in relative nobility of two metals or the alloy shows low anode efficiency, in an alloy plating bath, separate, soluble anodes of the two metals should be considered. The metal dissolution ratio and weight are controlled by carefully maintaining: (1) the current density on each of the two anodes by separate adjustment of current to the anode bus bars and by regula-

tion of submerged anode area; (2) the potential drop between the two different anodes; (3) the potential drop between the cathodes and each set of anodes; and (4) the proper placement or position of the anodes in the tank so that anodes on one bus bar do not receive series current flow from anodes on the other bar. In the two-anode bus bar setup shown diagrammatically in Fig. 6, the three voltages V_m , V_q , and V_{m-q} must be maintained within empirically determined ranges. This method of single metal anodes is being used successfully but requires more exacting control than that of alloy anodes, when they are usable.

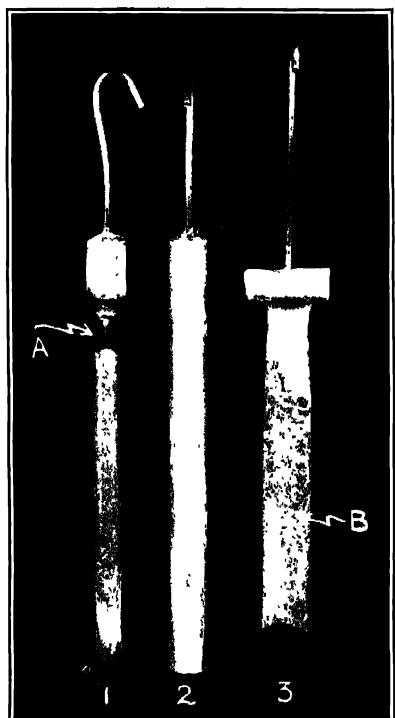
Figure 7 shows individual cadmium and silver anodes that were partially consumed in a two-anode system for depositing Ag-Cd alloy. At point A on cadmium anode No. 1 is a dark film which indicates that the cadmium anode current density was slightly too high, but was workable without chemical displacement of silver on it.

The idea of using individual anode control in alloy deposition is not entirely of recent origin.³³ However, successful pilot plant and commercial plant operation is very recent.^{36, 27, 84, 6}

Mechanical-mixture-type alloy anodes (type I in Fig. 4) have been used in deposition of Ag-Pb alloys, with plate reproduction

Fig. 7. Photograph of anodes that were used in a plating cell arranged according to Fig. 6. No. 1 is a cadmium anode after some use; 2 is an unused cadmium anode; 3 is a silver anode after use.

over long periods of operation.³⁴ Figure 8 shows the uniform dissolution of 3.8% Pb + 96.2% Ag anodes. In this case, an anode addition agent, i.e., sodium tartrate, aided the dissolution. It also assisted the deposition control. This illustrates a possible alternative to using individual soluble anodes, which is to use an anode addition agent when alloy anodes give trouble. Compounds that aid single-anode dissolution should be tried first to aid the alloy anode process.



The Ag-Pb alloy anodes of Fig. 8 consisted of two phases, a silver-rich solid solution and pure lead which segregated at the grain boundaries as shown by Fig. 9. This lead segregation causes intergranular weakness that appears to be characteristic of the thermally prepared alloy and is responsible for poor bonding when the alloy is cast on steel. It is apparent from Fig. 10 that the plated alloy from a bath using the anodes of Figs. 8 and 9 shows no lead segregation before or after annealing, which, however, caused recrystallization of the as-plated structure.²⁷

Brass anodes (Cu-Zn alloy of type V in Fig. 4) are used in baths depositing a brass of composition maintained within close limits.⁴⁵ In decorative brass plating, alloy anodes are widely used with process control designed to produce a certain plate color.

In oxalate Cu-Zn plating solutions, neither alloy anodes nor separate anodes maintained a steady copper concentration in the bath. A cyclic variation in plate composition resulted.⁸⁵ In cyanide baths, individual copper and zinc anodes were first attacked in proportion to their exposed areas. By suitable choice of area ratio (actually, anode current density adjustment), the proportion of zinc and copper can be easily controlled during long periods of electrolysis.

Bronze anodes^{84,86} (type V, Fig. 4) containing 90% Cu + 10% Sn were found to dissolve unsatisf-



Fig. 8. 3.8% Pb + 96.2% Ag anodes after appreciable use in alloy plating bath, giving reproducible results for depositing alloys of the same composition.

factorily in oxalate baths and to give a slime rich in tin. In cyanide baths, the bronze anodes dissolved cleanly and brightly, so that easy control of Cu-Sn concentration has been maintained in cyanide-stannate baths by bronze anodes (properly "filmed") during long periods of deposition.⁸¹ The anodes can be operated at 90% current efficiency, which depends on current density as shown by Fig. 11.

Separate anodes of tin and copper were used in oxalate bronze plating baths with individual current control for each anode bus.⁸⁷ If the

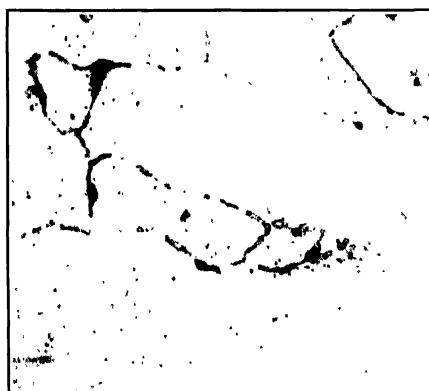


Fig. 9 Structure of the Ag-Pb alloy anodes of Fig. 8. Lead segregation along the grain boundaries is shown. There is some lead present as dendrite traces in the silver grains. (From Reference 30.)

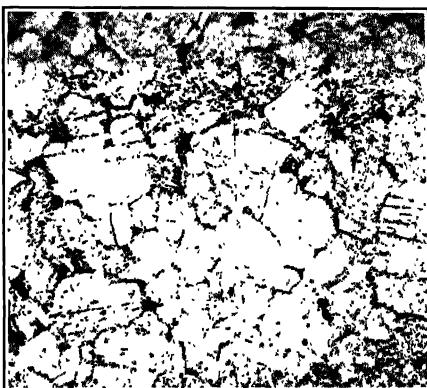
tin anode current density was too low, copper deposited on the tin anode. In a cyanide-stannate bath using separate anodes, tin plated on the copper anodes if operating conditions were incorrect. High tin anode current density was required in order to dissolve tin in the proper valence state, as in the case of stannate tin baths.

Plate compositions were reproduced in long periods of plating. In Cu-Sn alloys the intermetallic compounds are difficultly soluble, and the "speculum" composition is insoluble in operable cyanide-stannate plating baths. For speculum plating, copper and tin anodes are used.⁶ Intermetallic compounds also are likely to be insoluble as alloy anodes in other systems. When such insolubility is encountered, plating with periodically interrupted direct current, or with periodic reverse current, or with superimposed alternating current on the direct current can cause alloy anode dissolution in a manner compatible with alloy electrodeposition on the cathode. An anode depolarizing addition agent such as a fluoride or chloride can give assistance to the special current flow conditions.

- (A) As-plated alloy. Ductile plate having a Vickers pyramid hardness of 95 to 112. Random lead distribution. 1000 \times .



- (B) Plated alloy, as-annealed 1 hr at 220°C (550°F). Tough, ductile, having hardness of 45. Recrystallization has occurred. Lead still randomly distributed but has not segregated 1000 \times



- (C) Plated alloy after annealing for 3 hr at 220°C (550°F). Shows no bond weakness at the steel back (lower part of photomicrograph) nor evidence of lead segregation as seen in Fig. 9. 500 \times .



Fig. 10 Ag-Pb alloy deposited from a cyanide-tartrate bath using soluble Ag-Pb anodes of Figs. 8 and 9 (From Reference 37.)

Many thousand pounds of Ni-Co alloy anodes (type II in Fig. 4) are consumed in production plating of Ni-Co alloys.¹

The aforementioned references were selected from the few reports giving a relatively complete picture of anode operation in alloy plating. There are other records which, if taken as a group, bring out more detail in specific systems. The significant fact is that evaluation of soluble anode operation must be based on a clear understanding of the alloy itself, its possible impurities, and the type of bath. Alloy

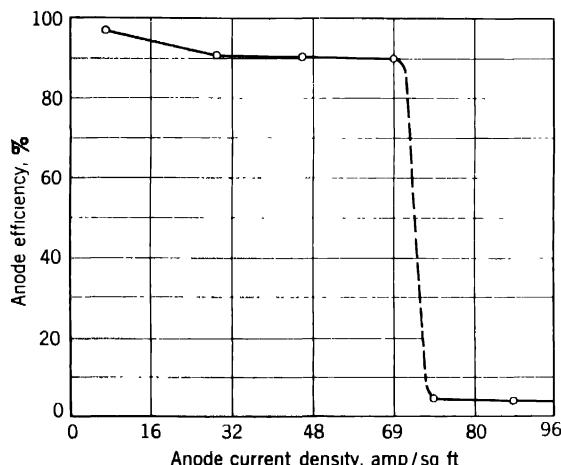


Fig. 11. Bronze (87.8% Cu + 12.2% Sn) anode current efficiency versus current density in cyanide-stannate baths. The large drop in efficiency at about 60 amp/sq ft was associated with film formation on the anodes. (From Reference 84.)

anodes do not necessarily dissolve completely, or in the same ratio or with the same efficiency that the metals are deposited from a given bath.

The third type of anode system, that of insoluble anodes, is used successfully in a few cases but introduces chemical control problems. Metal replacement can be made only by addition of soluble compounds of the metals to the bath. Buildup of undesirable anion concentration and change in pH are difficult to avoid unless oxides or carbonates (in acid baths) can be used to replace metals. Insoluble anodes are not recommended for use with heavy continuous production.

A modification of the insoluble anode system uses an anode of one metal only, the second metal being added as a soluble salt. This procedure is entirely suitable and is widely used when the second metal is relatively small in amount, as in the case of zinc addition to bright nickel baths, cobalt addition to Ni-Co baths (low cobalt content),

molybdenum to zinc baths, ZnO in brass baths. Except as governed by costs, anodic introduction of metal into the bath is preferred.

BATHS AND FUNCTIONS OF CONSTITUENTS

Because many bath compositions are possible, failure in one type in no way proves that deposition of a given alloy is impractical. The "primary ion ratio," M_1^{v+}/M_2^{v+} , is seldom equal to the "primary salt ratio" (primary salt refers to the metal salts used to introduce M_1^{v+} and M_2^{v+}), nor is the primary ion ratio necessarily equal to the ratio of activities, a_1^{v+}/a_2^{v+} , of the metal ions in the cathode film. These ratios are governed by the type of solution used. Since only a few metals have similar activities in simple salt solutions, alloy plating baths are, for the most part, based on complex ion formation which provides relatively very low actual concentration of M_1^{v+} and M_2^{v+} . The metal ratio in the plate will probably differ from the ratio of "metal salts" in the bath.

Alloy plating baths are generally of a type for which at least one of the metals can be deposited singly in good form. A few examples are: (1) Ni-Co,^{1, 88, 90} Ni-Zn,² and Ni-Fe^{91, 92, 17} from sulfate-chloride baths; (2) Cu-Zn,⁴⁸ Ag-Pb,¹¹ Ag-Cd,⁷⁹ Cu-Sn,^{26, 27} and gold alloys⁹³ from cyanide baths; (3) Pb-Sn alloys from fluoroborate baths;¹⁷ (4) silver, gold, and platinum alloys from complex halide baths.⁹¹

Promising alloy plating baths are those in which the metals to be codeposited are present in complex ions of different anion component. Common ion effects can then be selective for one or the other of the metals individually. Examples of this type of bath are those for Ag-Pb³⁴ and Cu-Sn^{84, 85, 87} alloys. Partial effects of selective common ion action are to be found in Cu-Zn and Cd-Zn baths. In the bath for Ag-Pb, the silver is in a cyanide complex. The lead is in an alkaline tartrate complex and not in a cyanide complex. In the Cu-Sn bath, copper is in a cyanide complex and tin is in a stannate complex. Therefore certain compounds can be added to these baths to alter the ion concentration of one metal with relatively little effect on that of the other. Free cyanide concentration affects silver and copper in the respective examples with relatively little effect on lead and tin. On the other hand, free cyanide concentration is very important in Cu-Zn plating because it affects both the copper and the zinc; yet in this case sodium hydroxide can be added with different result since zinc forms a zincate complex, whereas copper forms no analogous complex. A similar state exists for Cd-Zn cyanide baths, where cadmium

forms only cyanide complex and zinc forms cyanide and zincate complexes. An empirical knowledge of these relationships can appreciably reduce the experimental effort in developing alloy plating baths. Information on the ionization constants and ion mobilities is also important.

No alloy plating investigation should overlook the possibilities of nonaqueous organic electrolytes. They offer freedom from electrode-depositable hydrogen, and deposition potentials of the metals appear to be closer together than in aqueous solutions. Aluminum and its alloys are deposited from formamide solution;⁹⁵ Ni-Co from triethanolamine solution;⁹⁶ and aluminum from ethylpyridinium bromide solution.^{97, 98} Such electrolytes have special interest for plating the active metals, such as aluminum, magnesium, beryllium, and manganese, and the difficultly depositable metals, chromium, titanium, molybdenum, tungsten, zirconium, and their alloys.

In general, the constituents of alloy plating baths can be divided according to function: (1) the primary salts which provide the primary ions, M_1^{r+} and M_2^{s+} ; (2) other salts, secondary salts, which, by mass action effect, influence the ionization of the primary ion source; (3) addition agents controlling the form of the plate; (4) buffer compounds; (5) conductivity salts; and (6) salts promoting anode solubility. The function of each of these constituents in alloy baths is important as to effect on one depositing metal relative to its effect on a codepositing metal. For single-metal deposition, the above factors are combined only to achieve suitable physical properties of the plate, current efficiency, throwing and covering power, and anode solubility. Alloy deposition makes the same demands, to which are added uniform plate composition and dissolution of anode systems containing more than one metal. Anything unfavorable to the deposition of one of the metals is likely to be unfavorable to the deposition of the alloy, but not necessarily so.

THE PRIMARY AND SECONDARY SALTS IN THE BATH

The primary salts determine whether codeposition can be obtained. They are largely responsible for the ion activities of the depositing metals in the cathode film, since they determine the concentration and valence of the ions. Secondary salts are those of nondepositing metals with or without a common anion. These salts are necessary to improve conductivity or anode solubility or both, and influence the pH, ionic strength, and ionic mobilities in the cathode film.

ADDITION AGENTS AND BUFFER COMPOUNDS IN THE BATH

There is no entirely satisfactory definition of an addition agent.⁹⁹ Often specific influence is produced by addition agents of colloidal nature as well as by those which are in true solution. There might be little, if any, effect on the static electrode potential, but a marked effect to make deposition potentials more negative. As a result, alloy plate compositions and deposition efficiencies can be altered and the nature of soluble anode dissolution changed by addition agents.

In many cases no clear distinction can be made between bath constituents as to addition agent and buffer functions, since many substances act in both capacities. Their main function, when properly administered, is to produce sound metallic plates of desired physical properties under conditions which, without the addition agent, would result in powdery, brittle, or irregular deposits. The addition agent may be said to alter the limiting current density of one or both metals,* to change the polarization during codeposition, or to increase the current efficiency at the anode or cathode or both.

An addition agent can also influence the plate composition,^{21, 87, 100} especially if it forms complex ions with one or both metals. Addition agents effective in single-metal plating baths are likely to be effective in alloy plating baths of the same type.

For many years tartrates (or citrates) have been added to plating baths for improving anode dissolution and preventing hydrolysis of the primary metal salts. Amounts used varied up to about 6.7 oz/gal. Recent work discloses the use of citrate (or tartrate) in concentrations in excess of 26.8 oz/gal in tungsten alloy plating.²⁰

In alloy plating one can also think of the second metal as an addition agent influencing the structure and properties of the other. This is the viewpoint taken in the case of bright deposits involving two metals.

ANODE ADDITION SALTS

Addition salts, such as alkali chlorides, Rochelle salts, citrates, pyrophosphates, and fluorides, have the important purpose of promoting anode solubility of the metals in the desired ratio, at the required rate, and in the necessary valence form. These secondary salts increase the limiting current density for sludge-free dissolution. The choice of addition salts depends on the type of anion, i.e., sulfate, fluoride, cyanide, associated with the primary and secondary salts,

* Usually the limiting current density is determined by the more noble metal.

and on the metals to be dissolved. Materials effective in single-metal anode dissolution are the best first choice for alloy baths.

THE INFLUENCE OF THE COMMON VARIABLES IN ALLOY PLATING

The independently controllable variables, current density, agitation, temperature, *pH*, and concentration of bath constituents, influence the ratio in which two or more metals codeposit. They also influence the physical character of the plate and the rate of deposition. An appreciable change in any one variable may require an appreciable and compensating change in another variable or combination of variables in order to maintain the given ratio. No single variable can be discussed on the basis of an exact independent effect on the plate composition or physical properties, yet each variable can be considered with regard to its general effect. The relative nobility of the metals, as used herein, refers to the metal of more positive (or less negative) potential as being the more noble in a given type of electroplating bath.

THE EFFECT OF CURRENT DENSITY

An increase in current density tends to increase the proportion of the less noble metal in the alloy plate. The extent of change is likely to be greater in simple primary salt solutions than in complex primary salt solutions, and greater when the codepositing metals are in complex ions with common anion than when the anions of the complex ions are different. In the latter case, when the metals are associated with different complex ions, an appreciable change in current density can be permitted with little change in plate composition.^{32, 81, 87, 99}

The limiting current density for codeposition in commercially acceptable physical form is likely to differ from the limiting current density for codeposition without regard to physical condition. Since addition agents influence the physical properties of plates, limiting current densities can be altered by using appropriate addition agents. Agitation, temperature, *pH*, and the like also influence the current density effects. If addition agents are used, their influence on the plate composition must be considered when judging current density effects.

THE EFFECT OF AGITATION

An increase in agitation usually increases the amount of more noble metal in the alloy plate, thus tending to offset the effect of an increase

in current density. The primary ion ratio established at the cathode face in a still bath depends on the degree of ionization, the concentration of the primary salt or complex ion, the relative ion diffusion velocities at the given temperature, and, for some complex ions, the rate of ionization. By mechanically bringing fresh bath to the cathode film and decreasing the film thickness, agitation offsets the normal tendency for more rapid depletion of the more noble metal ions in the deposition zone.

The relative effect of agitation is likely to be less pronounced when the primary metal ions are associated with complex ions rather than with simple anions, and more pronounced when the two or more metals are associated with like anions rather than with unlike anions.

THE EFFECT OF TEMPERATURE

An increase in temperature usually tends to increase the proportion of more noble metal in the alloy plate, thus having the same effect as an increase in agitation and the opposite effect to an increase in current density. Temperature increase decreases the polarization, i.e., the term P in Eq. (2), of the more noble metal relatively more than the polarization of the less noble metal. Exceptions can be found in cases where the temperature effect on the degree of ionization and ion activity is relatively greater for the less noble metal. It is conceivable that temperature changes in either direction from an optimum value (or narrow optimum range) can reverse the relative nobility of two codepositing metals. In such cases, an increase in current density or in agitation will have a different effect on plate compositions deposited at different temperatures.

THE EFFECT OF pH

The influence of pH has been studied to a lesser extent than the other variables in alloy plating. The pH is generally accepted as a more important factor in physical property control than in plate composition control. This is particularly so in brass, Ni-Co, Ni-Zn, Cu-Sn, Ag-Pb, Pb-Sn, and Ag-Cd deposition.

There have been divergent reports on the effect of pH change on plate composition. The differences observed could be caused by the unintentional overlooking of the effect of a change in some other variable. Further studies are needed on the influence of pH on plate composition before a general trend, if any, can be stated, since changes in pH of the cathode film are so closely associated with the other variables.

A specific influence for *pH* is to be expected in determining the most efficacious addition agent, particularly where bright alloy plating is the goal.

THE CURRENT EFFICIENCY IN ALLOY PLATING

There are instances on record where the codeposition current efficiency exceeds that of single deposition of one or both metals from the type of bath in question. When this occurs, the current efficiency will depend on the alloy composition. For this reason the thickness distribution of an alloy plate might differ from that expected according to the current distribution.

The electrochemical equivalent weight in grams per ampere-hour of an alloy electroplate deposited at 100% current efficiency is given by the expression

$$W_{\text{alloy}} = \frac{W_1 \cdot W_2}{f_1 W_2 + f_2 W_1}$$

where W_1 = electrochemical equivalent weight of one of the metals in grams per ampere-hour, and W_2 is that of the other metal.

f_1 and f_2 are the weight fractions of the two metals, respectively:

$$f_1 + f_2 = 1$$

Alloy plating has effected codeposition of some metals not deposited singly; thus the current efficiency for that metal is raised from zero to some significant value.^{68-74, 76, 25}

THROWING POWER IN ALLOY DEPOSITION

In alloy plating, throwing power and covering power depend on the current distribution and the effect of current density on plate composition and current efficiency. Since current density change can alter the composition of an alloy plate, there is a question of uniform plate composition associated with throwing power. Whenever the plate composition is critically dependent on current density, the "throwing power of composition" will be critical. Fortunately, alloy deposition baths can be developed in many cases where the current density range is wide enough to permit a good throwing power of composition over fairly irregular shapes. A knowledge of current density effect on composition and current efficiency will give a good indication of expected throwing power, covering power, and plate composition uniformity over a surface for the particular type of bath being used.

THE INFLUENCE OF BATH CONCENTRATION IN ALLOY PLATING

The bath concentrations in alloy deposition are usually similar to those for the single deposition of the individual metals from the same type of bath. The concentration of primary salts and of secondary salts determines the concentration and activity of the primary ions and, therefore, determines the plate composition, as already pointed out. Since the essential conditions for alloy plating are based on ion ratios, dilution or concentration of the bath has an effect only as the ion ratios are changed. A change in ion ratios with dilution or concentration will depend on the relative effect on the degree of ionization, the primary salt concentration, and diffusion rates. The question of limiting concentration and of conductivity of the bath versus concentration is the same as for any metal deposition.

OPERATION OF ALLOY PLATING BATHS

Operating conditions and variables for alloy deposition in the several systems which are in large production, or which have been extensively studied in the laboratory, have ranges commercially practical to control. The actual operating values are in the same economic ranges as those of single-metal plating. The essential difference in control and reproduction in alloy deposition is that the operator must have a complete knowledge of how variations in temperature, current density, agitation, etc., within specified ranges affect the plate. Also, he must have an equally good understanding of the anode process.

BASIS METAL IN ALLOY DEPOSITION

Specifications for basis metal preparation cover the same procedure as used in single-metal deposition. There is no difference in mechanical, physical, and chemical cleanliness required. In the case of some metals receiving electroplates, an alloy can be deposited more readily than one or both of the individual metals.

The bond and structure of the plate will depend on pretreatment of the basis metal—whether the deposit goes on the “true” crystal structure of the basis metal or on some distorted or broken-up surface layer, such as that produced by polishing, grinding, sand blasting, or other cold working. In general, the composition of the basis metal has no large effect on plate composition. The initial plate on different basis metals may vary slightly in composition owing to overvoltage

effects. This difference will diminish as the plate becomes thicker. Some cases have been observed where a thin alloy plate on platinum consists, for example, of 10% $M_1 + 90\% M_2$, whereas, on copper, the same conditions deposited 9% $M_1 + 91\% M_2$. Such a small variation would usually have no practical significance on the phase structure or chemical properties of the plate, and would be relatively less the thicker the alloy plate.

There is evidence that alloy deposits, because of differences in deposition potentials, can give complete coverage of all crystal faces by the first few atomic layers of plate, whereas single metals give "selective" deposition on some crystal faces only, until appreciable plate thickness is reached.

Brass

LEONARD E. WEEG* AND HAROLD J. WIESNER†

Brass plating is employed primarily for one of two purposes: (1) to match the appearance of solid brass or bronze, or (2) to obtain adhesion of rubber to metal.

The early baths employed for decorative purposes have been described by Bennett.¹ Ferguson and Sturdevant² have studied the effects of varying plating conditions on cathode and anode potentials and efficiencies and on the composition of the deposit. Hogaboom has investigated the effect of sodium carbonate³ and the effect of pH changes.⁴ Pan⁵ has studied the nature of the metallic cyanide complexes. There are several references on the effect of ammonia in a brass bath⁶⁻⁹ and on methods of analysis^{10,11} for it. Heiman¹² and Heiman and Cotton¹¹ have studied methods for determining free cyanide and ammonia. Blum and Hogaboom¹² devote a section of their book to the subject of brass plating. Coats¹³ and Kronsbein and Smart¹¹ describe brass plating for rubber adhesion. Other papers relate factors governing the degree of adhesion¹⁵⁻¹⁸ and the nature of the rubber to brass bond.^{19,20} A rather comprehensive paper by Coats²¹ covers the general subject of brass plating. During the World War II period, brass plating was employed extensively on steel shell cases.¹⁴

Clarke and co-workers⁸ patented the use of an organic amine as a substitute for ammonia. There is a proprietary high speed brass bath.²² Oplinger^{23,24} reports a "white" brass solution—for depositing an alloy of 28% Cu and 72% Zn. A method of obtaining a bright brass finish on any basis metal is described by Beyer.²⁵

Much interest has been shown recently in "white" brass deposits, originally reported by Oplinger.²³ Saltonstall⁴⁵ concluded that a bright white brass deposit is an inferior substitute rather than a satis-

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factory alternate for a bright nickel deposit. However, for certain mild exposures there are a number of applications, such as toys, tubular furniture,⁴⁶ tools, novelties, interior automotive hardware and trim,⁴⁷ and picture frames, in which white brass plating gives adequate protection, particularly when coated with a lacquer.

Periodic reversal of current⁴⁸ (PR plating) is being applied in production brass electroplating to improve smoothness and plate distribution. Some increase in brightness has also been obtained.

PRINCIPLES

Although brass may be deposited from other types of solutions,^{26, 27} present commercial baths are cyanide solutions. The composition and operating conditions may be varied over wide ranges to give deposits of almost any copper:zinc ratio. Changes in such factors as the copper:zinc ratio in the electrolyte, pH, temperature, and current density markedly affect the composition of the deposit, and usually these factors must be controlled within fairly narrow limits. Anode composition also is important, since, for any given solution, an anode alloy must be chosen that will maintain the proper ratio of copper and zinc ions in the bath.

For decorative purposes, the composition of the deposit is secondary to the color obtained. Ferguson and Sturdevant² observed that the copper:zinc ratios in the twenty brass solutions recommended in the literature and compiled by Bennett¹ varied from 10:80 to 10:1. Although all apparently gave a yellow brass deposit, the composition of the deposit varied as much as the metal ratio in the electrolytes. The effect of ammonia in producing a yellow color is very pronounced and will be discussed later.

For the most part, brass solutions are compounded to give a deposit with a copper:zinc ratio of 70:30 to 80:20. In baths which produce deposits within the above-mentioned range, the metal ratios (Cu:Zn) of the electrolytes may be 33:67,^{8, 14} 60:40,²² 75:25,¹³ 80:20,²⁸ or even 95:5.²⁴ Graham⁴⁹ has investigated the plating of high copper-zinc alloys.

The composition of brass applied to steel for rubber bonding is critical. The copper content must be between 72 and 78% if the rubber compositions employed are ordinary stocks and do not include ultra accelerators such as zinc dithiocarbamate.²⁹ Additional qualities of the brass deposit are also required.²⁹ The total of impurities in the deposit should not exceed 2%, and there should be no more than a trace of any one of them. The deposit should also be free from substances

arising from mechanical codeposition of ammonia-ferrocyanide complexes. These complexes have been identified by electron diffraction patterns.³⁰

The minimum thickness of deposit recommended by Zentler-Gordon and Roberts²⁹ for rubber adhesion is 0.0001 in. However, Coats¹³ gives a much lower value (0.00002 in.).

BATH COMPOSITION AND FUNCTIONS OF THE CONSTITUENTS

The initial compositions of some of the baths which have been reported in the literature are given in Table 1.

TABLE 1. BRASS PLATING BATHS

	1938 (Pan ^b)		1941 (Coats ²¹)		1944 (Kronsbem and Smart ¹⁴)		1947 (Hogboom, J and Hall ²⁸)	
Copper cyanide, CuCN	oz/gal	g/l	oz/gal	g/l	oz/gal	g/l	oz/gal	g/l
Equiv-Cu	4.1	30.9	3.5	26.2	2.8	21.0	4.0	30.0
Zinc cyanide, Zn(CN) ₂	2.9	21.9	2.5	18.5	2.0	15.0	2.8	21.0
Equiv-Zn	1.6	11.1	1.5	11.3	7.2	53.8	1.25*	9.4
Cu/Zn ratio	0.83	6.2	0.83	6.3	4.0	30.0	0.7	5.25
Total sodium cyanide	3.5	3.5	2.9	2.9	0.5	0.5	4.0	4.0
Free sodium cyanide *	6.9	51.3	6.0	45.0	9.5	10.2	71.8-75.8	7.5
Sodium carbonate	1.1	8.2	1.0	7.5	0.54-1.1	4.0-8.0	2.0	15.0
Ammonium hydroxide, sp. gr. 0.9	4.2	31.5	None added		2.7	20.0	4.0	30.0
pH	Not given		10.3-11.0		12.6-12.8		Not given	
Temp., °C	21-22		27-35		55-60		24 38	
Temp., °F	70-72		81-95		131-140		75-100	
Cathode c.d., amp/sq ft	2-20		9.3		20		3-5	
% Cu in anodes	85		75		70		80	

* Sodium cyanide in excess of that required to form Na₂Cu(CN)₃ and Na₂Zn(CN)₄.

Copper and zinc cyanides are present for the purpose of supplying metallic ions in solution. Since these salts are practically insoluble in water, they must be dissolved in sodium or potassium cyanide solutions. The earlier baths described by Bennett¹ employed such compounds of copper and zinc as the carbonate, hydroxide, sulfate, and acetate. These were mixed with water, and potassium cyanide was added until a clear solution was obtained. Such practice is dangerous because of the evolution of cyanogen. Furthermore, objectionable anions may be introduced. In modern practice, cuprous cyanide and zinc cyanide are commonly used.

Brass cannot be electrodeposited commercially from the simple salts of the two metals since their potentials are too far apart. The addition of sodium cyanide (or potassium cyanide) to a solution containing copper and zinc ions causes the potentials of both metals to become more negative. However, the potential of the copper ion (with respect to a standard electrode) becomes negative to a greater degree than does that of zinc. One function of the sodium cyanide, then, is to bring the deposition potentials of the copper and zinc ions together, thus making Cu:Zn alloy deposition possible.

Sodium cyanide serves to form water-soluble complexes with the copper cyanide and zinc cyanide. Most authors regard the sodium cyanide in excess of the theoretical amounts required to form the complexes $\text{Na}_2\text{Cu}(\text{CN})_3$ and $\text{Na}_2\text{Zn}(\text{CN})_4$ as free sodium cyanide. Table 1 shows that the free cyanide values range from 0.54 to 2.0 oz/gal. The free cyanide is necessary to maintain good anode corrosion, to improve conductivity, and to prevent blistering of the brass deposits. Clarke et al.,⁸ using Pan's bath,⁶ found that 0.67 oz/gal was sufficient to prevent blistering. In general, as the free cyanide is increased, the cathode efficiency decreases. There is also a decrease in the copper content of the deposit.

Sodium carbonate may be added to brass baths to provide buffer action at a pH of about 10.3 (colorimetric). It has little effect upon the conductivity of the bath. In baths used for plating brass for rubber adhesion, the carbonate is not always added. Sodium hydroxide may be added in small amounts to raise the pH of the bath. The OH^- ion has little effect on the dissolution of the anodes, but it is important in decreasing the resistance of the bath and in controlling the zinc ion concentration, with a resulting increase in the zinc ratio of the deposit.²¹

An ammonia or ammonium salts are sometimes added to brass baths to improve the color of the deposit, particularly in decorative plating. The effect of relatively small amounts (0.2–1.5 g/l) in correcting off-color deposits is remarkable. The exact mechanism by which the ammonia accomplishes this result is not entirely agreed upon.^{6,11} However, several authors^{6,7,8} have noted an increase in the zinc content of the deposit with an increase in ammonia content. A slight increase in cathode efficiency accompanies such additions.

Kronsbein and Smart,¹⁴ in operating their bath at elevated temperatures (55° to 60°C), found that the ammonia content (due to decomposition of sodium cyanide) reached a stable concentration of about 0.4 g/l, and no additions were required.

Clarke and Bradshaw³¹ found monoethanolamine a satisfactory substitute for ammonia in a bath operated at elevated temperatures. The relatively low volatility of this organic amine under these conditions was considered advantageous. A concentration of 1.3 oz/gal of monoethanolamine gave results similar to those obtained with 0.13 oz/gal of ammonia. The related compounds, di- and triethanolamine, were ineffective.

The use of other addition agents in brass baths to control the color and to give smooth deposits is described by Coats.^{13, 21} Arsenic, in the form of arsenous oxide (As_2O_3) may be dissolved in sodium hydroxide and added in small quantities. When deposits are red from a high copper content, the addition of about 0.001 oz/gal of arsenic will correct this condition. An excess of arsenic is to be avoided, since large additions cause the deposit to have a "pasty-white" appearance. Nickel in a brass bath behaves similarly to arsenic, and phenol (0.4 oz/gal) is sometimes added to decrease the zinc content of the deposit.

Weiner³² discloses a bath containing zinc, copper, and alkali metal cyanides, a polyvinyl compound, and a thiocyanate (0.05–40 g/l) of one of the metals of the eighth group of the periodic system and 0.1 to 5.0 g/l of gelatin. Another patent³³ covers the use of ketone-aldehyde polymerization products in potassium cyanide baths for the electrodeposition of bright layers of brass, copper, zinc, and cadmium. Stabrovskii³⁴ employs sodium oxalate (3.5 oz/gal) and gelatin as addition agents.

BATH OPERATION

CURRENT DENSITY

Much brass plating is done at relatively low cathode current densities, about 5 amp/sq ft. There has been a definite trend to develop baths^{6, 14, 22, 23, 35} employing higher cathode current densities, up to 50 amp/sq ft. Anode current densities are kept at a low value, about 5 amp/sq ft.

The reported effects of increasing the cathode current density on the composition of the deposit vary with different workers. Coats,¹³ Pan,⁶ and Clarke⁸ state that the percentage of copper in the deposit is increased with an increase in cathode current density, whereas Ferguson and Sturdevant,² Blum and Hogaboom,¹² and Hogaboom, Jr.,²⁸ have reported the opposite effect. This apparent discrepancy can be explained when one realizes that the relative nobility of copper and zinc in cyanide brass plating baths is not fixed but varies with the conditions of deposition.

BATH TEMPERATURE

The bath temperature may be varied to produce the desired composition or color of the deposit. Increasing the temperature 2.8°C may lead to a 3% decrease in the zinc content of the deposit. Therefore accurate brass plating requires close temperature control, preferably of the order of $\pm 0.5^{\circ}\text{C}$. Increasing the bath temperature increases the cathode efficiency and permits the use of higher current densities with attendant increase in the rate of deposition. Many brass baths are operated at "room temperatures," some at 27° to 35°C, and some at 50°C.

pH RANGE

Brass may be plated at pH values in the range from 8 to 13 (colorimetric values). Hogaboom⁴ studied the effect of pH in the range 8.2 to 13 on composition of deposit and on cathode and anode efficiencies. Several indicators are available for determination of pH within this range, such as Alizarine Yellow C.G.⁸ (pH 9.5 to 11.5) and Tropaeolin O (pH 11.2 to 12.8).

The electrometric method for pH control, using the high alkaline, Beckman type-E glass electrode and pH meter, has been found satisfactory by Gray.¹⁰ The glass electrode method is not subject to errors because of difference in eye sensitivity, and the pH values obtained are not affected by many materials present in plating baths, such as colloidal substances, dissolved organic compounds, and oxidizing and reducing agents. The glass electrode in a brass solution having a pH of about 12 gives readings approximately 0.4 pH unit lower than those found by colorimetric methods. pH papers were found to agree closely with the glass electrode readings, and they can be recommended.

Increasing the pH increases the percentage of zinc in the deposits. If the plater is troubled with a "high-copper-red" deposit, he may obtain the desired yellow brass color by increasing the pH by adding caustic soda or ammonia. (Either high copper or high zinc will cause a red deposit, and it is not possible to tell from the color which it is.) Ammonia will elevate the pH only when it is quite low; thus, at a bath pH of 11.5 or above, ammonia will not raise the pH. If the trouble is a "high-zinc-red" deposit, sodium bicarbonate will correct it. Some platers employ other weak acid salts such as sodium bisulfite, or weak acids such as boric acid. These are not safe to use because they may evolve poisonous hydrocyanic acid (HCN) gas from

the bath. If used, they should be dissolved in water first and introduced cautiously into the bottom of the tank through a glass tube.

CURRENT EFFICIENCY

The cathode efficiency is comparatively low (75%) in most brass baths, and, depending upon the conditions of operation, it may vary over wide limits (55 to 95%). Cathode efficiency may be increased by: reducing the free cyanide to the minimum value consistent with good anode corrosion; maintaining a high metal concentration; raising the bath temperature; decreasing the current density; decreasing the pH; adding arsenic, citrates, or tarbrates; and by thoroughly cleaning the work.¹³ The higher the percentage of copper in the deposit, the greater will be the weight of brass deposited with a given number of ampere-minutes. This results from copper being monovalent and zinc being bivalent in cyanide solutions.

Anode efficiency may be increased by keeping the current density low (5 amp/sq ft); using agitation; heating the solution; increasing the free cyanide; decreasing the total metal content; increasing the percentage of copper in the anodes; reducing anode impurities such as tin, nickel, and arsenic; minimizing the concentration of bath impurities such as sodium ferrocyanide, silicates, and chlorides; and maintaining the concentration of sodium carbonate below 10 oz/gal.

When the above recommendations are followed, anode efficiencies of 95% may be obtained. Under these conditions and when anodes of the proper composition are used, little or no additions of copper and zinc cyanide are necessary. A white film on the anodes is generally zinc cyanide, and it indicates that the free sodium cyanide content is too low. In baths containing arsenic, a steel-gray film which dissolves when the current is turned on is usually elemental arsenic. Arsenic can be removed by immersion deposition on sheet copper. A brown-to-black, non-conducting film which does not disappear when the current is turned on is generally lead. A loosely adherent, dark, conducting film is cupric oxide and does no harm. Tin in the bath will polarize anodes with the formation of a white film, and will darken the brass deposit. Tin can be removed by adding calcium chloride, which precipitates calcium stannate.

THROWING POWER

The throwing power of brass cyanide solutions is high. However, in remote areas of the article being plated and in recesses, the brass de-

posit may be pink owing to a high zinc content. As an example, a steel stamping about the size and shape of a large tea cup, was found to be plated with red brass containing 45% Zn on the inside, while on the outside the plate was yellow brass containing 30% Zn. Also, the brass layer was thinner on the inside of the cup than on the outside.

The throwing power is improved by increasing the free cyanide; by increasing the distance or spacing between cathode and anode; by using a still rather than an agitated bath, a low total metal content, a high current density, and a low pH; and by decreasing certain impurities in the bath.

ANODES

The use of brass anodes of the same Cu:Zn ratio as that desired in the deposit is recommended. Anodes with the following percentages of zinc have been successfully employed: 20, 25, 30, and 35.

The use of separate zinc and copper anodes is not recommended, because copper deposits on the zinc, and maintenance of the correct Cu:Zn ratio in the bath is not practicable.

In plating units where adequate space is available and the anodic current density may be held at 5 amp/sq ft or less, cast anodes may be used. In other units such as some automatic and barrel plating tanks, cold-worked (cold-rolled) anodes are recommended because they will corrode faster than anodes which have not been cold-worked.

The following specification may be used for brass anodes:

	Per Cent		Per Cent
Copper	75 ± 2	Tin	0.005 max.
Zinc	25 ± 2	Antimony	0.005 max.
Nickel	0.005 max.	Lead	0.005 max.
Arsenic	0.005 max.	Iron	0.010 max.

Similar specifications with regard to impurities may be used for the metal cyanides. When the current is off, brass anodes do not corrode rapidly enough in the bath to cause trouble. Anions to induce anodic dissolution are not necessary.

PREPARATION OF THE BASIS METAL

Preparation of steel for brass plating follows the usual practice for cyanide baths. If the part is to be plated for rubber adhesion, no buffing is required. Grease may be removed in alkaline solutions or by vapor degreasing. Pickling will remove scale, and an "over pickle" is recommended. The carbon smut may be removed by anodic treatment

in cold 50% sulfuric acid, by a reversing cyanide strip, or by tumbling in warm cyanide solution. Brass plate will tarnish if left too long in water that is too hot. The plated work should be quickly dried and stored in a dry place to prevent tarnish. It may be lacquered to prolong the time before corrosion occurs.

It is difficult to plate brass directly on gray and malleable cast iron, aluminum, and stainless steel. A cadmium strike on gray and malleable cast iron is recommended. Brass has been plated directly on aluminum and its alloys;³⁷ it can also be deposited, but with less satisfactory results, over a nickel undercoat. By special hydrochloric acid depassivation, stainless steel can be brass plated, but not very satisfactorily. Zinc die castings require an entirely different cleaning than steel.

Copper strikes make it impossible to determine the Cu:Zn ratio in the deposited brass and hence must not be used if the deposit is to be analyzed.

The first brass film deposited on steel is high in zinc.¹³ Each succeeding layer of brass deposited contains less zinc until a thickness of about 0.00013 in. (3.3 μ) is reached.

Capillary spaces, such as are found in lap welds, wire cable, and porous castings, will trap cyanide solution from the plating bath and cause "cyanide spots" ("spotting out"). Entrapped cyanide can be eliminated, but the operation is tedious and costly. It is cheaper not to plate such work. Castings can be made sound and assembly designs can be so made as to eliminate capillary spaces. In cables the individual wires should be plated before stranding. Alternate dipping in cold and hot water and centrifuging and washing in alcohol help somewhat in overcoming cyanide spots.

MAINTENANCE AND CONTROL

If the article to be plated is properly cleaned and the brass anodes are of proper purity, very little filtration of the bath is required. If copper and zinc cyanide additions are required, they should be dissolved and the solutions filtered before being added to the bath. If time and an extra steel tank are available, settling followed by decanting may be substituted for the filtering. Otherwise a plate and frame filter press, with the cloth coated with "filter aid" (infusorial earth) or with activated carbon, can be used to clarify the cyanide solutions before they are added to the bath. Continuous filtration is not necessary. Any white, milky precipitate should not be filtered off, since it is usu-

ally zinc cyanide and may be redissolved by adding a little sodium cyanide, heating, and agitating the bath.

The plating solution should be pumped out at intervals and the tank thoroughly cleaned to remove all foreign matter. At such a time the tank and the steel heating and cooling coils should be examined for grounds and leaks.

The tank, valves, filter press, and all parts that come into contact with the brass plating solution should be made of ferrous metal (steel, gray or malleable cast iron) and not of copper alloys, brass, or bronze. The tank is preferably lined with rubber in order to eliminate slow accumulation of sodium ferrocyanide, an undesirable impurity.

New baths operate better after a period of electrolysis. Freezing out of sodium carbonate has been found unnecessary for brass baths that have been operated continuously for over fifteen years. If the *pH* of the bath is held low, the solution drag-out and water drag-in will keep the carbonate below the concentration that causes trouble, which is usually 10 to 15 oz/gal.

Small, frequent additions of sodium cyanide are recommended—about 5 lb for every 1000 sq ft plated. The only other additions recommended are those necessary to maintain the *pH* within the desired range. When necessary, the *pH* may be increased with sodium hydroxide or decreased with sodium bicarbonate, each of which salts should be dissolved in water before being added. It is desirable to warm the bath to speed up the reaction of the sodium bicarbonate.

PHYSICAL CONTROL

The *pH* should be measured and adjusted, if necessary, every day. When brass is deposited for rubber adhesion, a plated sample should be tested for rubber adhesion each day. The specific gravity of the bath may be taken with a hydrometer to detect undue dilution.

The throwing power may be tested with a steel block containing ten holes, 0.5 in. in diameter and varying in depth from 0.15 to 1.50 in. The deepest hole that is covered on the bottom is a measure of the throwing power. The depth of this hole is usually about 1.35 in.

TESTING OF DEPOSITS

The thickness of brass plate may be determined as described below under "Analytical Methods," or it may be approximated on ferrous metal by a spot-test solution consisting of 1% sulfuric acid and 1% potassium ferrocyanide. A drop is placed on the brass plate with a

stirring rod. The number of seconds required for the spot to turn blue is a rough measure of the thickness. Brass plate of 0.00002 in. (0.5 μ) thickness will turn blue in about 10 sec at room temperature (20° to 25°C).

No thicknesses for decorative plate have been recommended by the American Electroplaters' Society or by the American Society for Testing Materials, but the general range is from 0.001 to 0.0005 in.; 0.00002 in. is near the minimum required for rubber adhesion.

The experienced inspector will be able to detect rather quickly any change in the color of brass deposits. With a daylight lamp he will readily observe pink, white, gray, dull, or thin brass. A thin brass coating usually reveals the steel underneath.

ANALYTICAL METHODS

The frequency of analysis of the solution and of the deposit is governed largely by the purpose for which the plating is being done and the volume of work being processed. In general, where brass plating is done for rubber bonding, an analysis of the deposit once a day is recommended.

Copper and zinc determinations on the bath should be run once or twice each week. At these intervals the free cyanide may also be determined or calculated. Ammonia determinations may also be made once a week in baths employing ammonia as an addition agent.

COPPER

Several methods for the determination of copper in brass plating solutions have been outlined in the literature. Miceli and Mosher³⁸ deposit brass on a platinum gauze from a sample of the bath to which a supporting electrolyte of ammonium sulfate and ethanolamine has been added. The brass deposit and platinum gauze are then weighed, the brass is stripped in a sulfuric-nitric acid solution, and the copper is deposited and weighed. The zinc may then be obtained by difference. Recently a polarographic method²⁹ was described for the determination of copper in brass solution and in brass deposits.

Electrolytic Method for Copper. 1. To 10 ml of filtered brass solution in a 400-ml casserole in the hood, add 10 ml nitric acid (sp. gr. 1.42) and 5 ml sulfuric acid (sp. gr. 1.84), cover with a triangle and watch glass, and carefully evaporate to dryness.

2. Bake for 20 min, take up in water, make alkaline with ammonia, boil, filter off iron hydroxide through a Whatman No. 41 filter paper, receiving the filtrate in a 200-ml, tall form beaker, and wash the pre-

cipitate *thoroughly* with hot, ammoniacal water. Unless the iron is to be determined, reject the precipitate.

3. Neutralize the filtrate with 1:1 sulfuric acid, then add 10 ml in excess.

4. Dilute (if necessary) to a volume sufficient to cover the gauze portion of the platinum cathode when the beaker is placed in position to electrolyze. (The cathode gauze has an area of 31 sq in.)

5. Start the stirrer, begin the electrolysis at 0.5 amp until the cathode is completely covered with a deposit of copper, then increase the current to 1 amp.

6. At the end of 15 min, raise the solution level to see if any more copper plates out on the platinum cathode stem. If not, stop the stirring and, with the current on, wash the deposit while lowering the beaker, receiving the wash water in the beaker.

7. Wash the deposit with water, then with alcohol, dry in oven at 105°C for 3 min.

8. Cool and weigh, strip the deposit in hot 25% nitric acid, wash and dry it as before, then cool and weigh it.

The weight of deposited copper times 18.82 equals ounces per gallon of copper cyanide (CuCN).

Volumetric Method for Copper. 1. Pipette a 10-ml sample into a 250-ml Erlenmeyer flask.

2. Add 5 ml of concentrated sulfuric acid (sp. gr. 1.84) and $\frac{1}{2}$ ml of concentrated nitric acid (sp. gr. 1.42) from a 10-ml graduate *while shaking under a hood*. (This operation must be carried out under a well-ventilated hood because poisonous hydrogen cyanide fumes are evolved.) Boil until dense white sulfur trioxide (SO_3) fumes are given off.

3. Cool and add 100 ml of distilled water.

4. Add concentrated ammonium hydroxide (sp. gr. 0.902) until the solution is colored a dark blue, and boil for 15 min.

5. Add 10 ml of 30% acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) solution. The solution should be colored light blue.

6. Cool to room temperature, add 25 ml of 20% potassium iodide (KI) solution, and shake.

7. Titrate with standard sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) solution until the brown color begins to turn yellow.

8. Add 2 ml of 1% starch solution, prepared by making paste of 1 g of starch with very little water and adding it to 100 ml of boiling water, and continue titrating until the blue color disappears for about 1 min.

The thiosulfate is standardized as follows: Dissolve 25 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 1 l of water. Weigh out 0.20 g of pure copper wire and

dissolve in 1:1 nitric acid. Add 5 ml of concentrated sulfuric acid (sp. gr. 1.84) and boil until sulfur trioxide fumes are evolved. Cool, add 100 ml of distilled water, and add ammonium hydroxide until the solution turns a deep blue color. Add 30% acetic acid solution until the color changes to a light blue or bluish green. Cool, add 25 ml of 20% potassium iodide solution, shake, and titrate with the thiosulfate solution as in 7 and 8 above.

The metallic copper (Cu), in ounces per gallon, equals $(2.67 \div \text{ml thiosulfate required for } 0.20 \text{ g of copper}) \times (\text{ml thiosulfate solution required for sample of solution})$. The figures in parentheses represent the factor for the standard thiosulfate solution. Ounces per gallon times 7.5 equals grams per liter of copper.

ZINC CYANIDE

Volumetric methods for zinc are given by Miceli and Larson³⁹ and Clarke et al.⁴⁰ The method described by Clarke is applicable only in the absence of ferrocyanide from the plating bath.

If the electrolytic method for the determination of copper is used, the zinc may then be titrated in the solution remaining: Add 3 drops of diphenyl benzidine indicator (1 g dissolved in 100 ml of concentrated sulfuric acid). Titrate with 0.05 N potassium ferrocyanide solution which has been standardized against a sample of high purity zinc oxide.⁴⁰ The color changes from purple to pale green at the endpoint.

Grams per liter of zinc cyanide equals milliliters of 0.05 N potassium ferrocyanide times the factor for the standard zinc solution.

FREE SODIUM CYANIDE

The analysis of brass baths is complicated by the fact that zinc may exist in the bath either as the zincate or as the complex zinc cyanide. The proportion of the zinc in the zincate is a function of the alkalinity of the solution, although no quantitative relationship has been established. For this reason it is difficult to analyze directly for free cyanide in brass solutions. If rigid analytical conditions are set up for any given bath, an empirical value by direct titration will be useful for control purposes, although it may not represent the true free cyanide content of the solution.

Pan⁴¹ recommended a direct titration method for free cyanide. McNabb and Heiman,⁴² in studying the method, showed that such factors as pH and temperature affect the results obtained by this method. However, they concluded that, of the methods reported in the literature for the analysis of free sodium cyanide in brass plating solutions, the method investigated by Pan was the most satisfactory.

They further state, "This method will yield reproducible and useful values only if the limits imposed by the sodium carbonate and ammonia concentrations are realized, and if the dilution, temperature, and *pH* are carefully controlled."

Clarke et al.⁸ found that Pan's method gave variable results according to the *pH* of the solution. They adopted, in general, the method described by Heinman and McNabb.¹¹ This consists, briefly, in adding an excess of caustic to a sample of the bath, thus tying up the zinc as zincate and releasing the sodium cyanide equivalent of the $\text{Na}_2\text{Zn}(\text{CN})_4$. This cyanide and the free sodium cyanide may then be titrated with standard, 0.1 *N* silver nitrate solution. The sodium cyanide combined as $\text{Na}_2\text{Cu}(\text{CN})_3$ is not affected. The procedure is as follows:

1. Pipette a 5-ml sample of the brass solution into a 250-ml Erlenmeyer flask.
2. Add 20 ml of 20% sodium hydroxide solution, 20 ml of 10% potassium iodide solution, and 40 ml of water.
3. Titrate with standard 0.1 *N* silver nitrate to the appearance of a bluish opalescence.

The free sodium cyanide is calculated as follows:

$$(\text{ml } 0.1 \text{ } N \text{ AgNO}_3) \times 1.96 = \text{free NaCN} + \text{NaCN equivalent to the} \\ \text{Na}_2\text{Zn}(\text{CN})_4$$

Call this value *A*.

Determine zinc by method outlined above:

$$\text{Zinc content (in g/l)} \times 3.0 \text{ gives NaCN equivalent to } \text{Na}_2\text{Zn}(\text{CN})_4$$

Call this value *B*.

Free NaCN (in g/l) is given by *A* - *B*.

The error of this method is about 2%.

Coats²¹ recommended determining the total cyanide by the distillation method, the copper and zinc by the methods given above and then calculating the free cyanide, assuming the complexes to be $\text{Na}_2\text{Cu}(\text{CN})_3$ and $\text{Na}_2\text{Zn}(\text{CN})_4$.

DISTILLATION METHOD FOR TOTAL SODIUM CYANIDE

Place 25 ml of 10% (by weight) sodium hydroxide in a 400-ml beaker; the 400-mm Allihn condenser should be washed with this solution; adjust the adapter so that the tip dips below the surface of the sodium hydroxide solution. (The tip of the adapter is fire-polished to a small opening to reduce the size of the escaping gas bubbles.) Into the 500-ml, side-neck distilling flask, introduce 5 ml of filtered plating

solution (use rubber bulb connected to pipette with a short piece of rubber tubing). By means of a separatory funnel add 200 ml of water containing 12.5 ml hydrochloric acid (sp. gr. 1.18). Heat the solution until all but about 75 ml has distilled over, disconnect the distilling flask, wash the condenser and adapter, receiving the washings in the beaker. Add 3 ml of 10% potassium iodide solution to the distillate and titrate with 0.1 *N* silver nitrate solution to the first permanent turbidity. Ounces per gallon of total sodium cyanide equal milliliters of silver nitrate used, times the factor, which in this case is about 0.26.

The method of standardizing the silver nitrate solution is to make up approximately 0.1 *N* sodium cyanide solution which is carefully checked against exactly 0.1 *N* silver nitrate solution (using the purest crystals of silver nitrate and glassware calibrated by the National Bureau of Standards). The silver nitrate solution used for titration of the cyanide distilled from the brass solution is then standardized against this standard sodium cyanide.

AMMONIA CONTENT

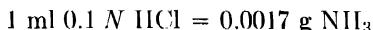
The determination of ammonia in brass baths has been the subject of several papers.^{7, 10, 11} Clarke et al.⁸ also outlined a procedure for this determination. They all involve distillation of a sample of the brass solution in the presence of an excess of alkali after the cyanides have been removed.

Heiman and McNabb¹¹ used the residue remaining from the determination of total cyanide by the distillation method. After cooling the flask to room temperature, 70 ml of 10% sodium hydroxide solution was added to the Kjeldahl flask and the ammonia was distilled into an Erlenmeyer flask containing 80 ml of 4% boric acid solution. The receiver was kept in an ice bath, and the distillation was carried out for 45 min. The condenser and distributor were rinsed, and the ammonia was titrated with 0.1 *N* HCl solution, methyl red being used as an indicator.

Blow et al.¹⁰ distinguished between "free" ammonia and other non-cyanide nitrogen compounds such as urea and cyanates. Methods were developed for the separate determination of free ammonia and total non-cyanide nitrogen. An accuracy of 0.02 g/l is claimed for the free ammonia determination. These authors claim that the method proposed by Monawec⁷ gives an ammonia value which is the same as the total non-cyanide nitrogen by their method.

The method of Clarke et al. gives ammonia values close to those of Blow et al. Clarke's method follows.

1. In a well-ventilated hood acidify 25 ml of the bath to litmus with acetic acid. Dilute to 100 ml.
2. Add 10% silver nitrate solution with stirring until no further precipitation occurs. This precipitates all the cyanide. If cyanates are present in the bath, they are precipitated by the addition of the silver nitrate solution, so no interference is encountered.
3. Filter the liquid into a Kjeldahl flask.
4. Set up the Kjeldahl flask with condenser and an adapter dipping into 50 ml of 0.1 *N* hydrochloric acid solution.
5. Add 10 g sodium hydroxide to the Kjeldahl flask, quickly close off, and distill off the ammonia. (Approximately one-half the volume is distilled over.)
6. Back titrate the hydrochloric acid solution with 0.1 *N* sodium hydroxide solution, using methyl red as indicator.



DETERMINATION OF COPPER-ZINC RATIO IN BRASS DEPOSIT

Reagents.

1. Ammonium persulfate solution.

$(\text{NH}_4)_2\text{S}_2\text{O}_8$ crystals	75 g
NH ₄ OII(sp. gr. 0.9)	335 ml
H ₂ O	665 ml
2. Sulfuric acid 1:1.
3. Diphenyl benzidine.
 1.0 g diphenyl benzidine in 100
 ml sulfuric acid (sp. gr. = 1.84).
 Keep in dark-colored bottle.
4. Potassium ferrocyanide solution 0.05 *N*.

$\text{K}_4\text{Fe}(\text{CN})_6$	22.0 g
$\text{K}_3\text{Fe}(\text{CN})_6$	0.30 g
H ₂ O	1000 ml

Procedure. Remove the brass deposit by immersing in cold ammonium persulfate solution. (If the sample has been cut for convenience in stripping, carefully remove any loose burrs or other particles of steel, as they will throw out metallic copper in the boiling solution.) After the brass has dissolved, remove the steel and wash with dilute ammonia water. Transfer to a hot plate and boil to reduce the volume at least 50% and to destroy ammonium persulfate. Filter off ferric hydroxide, washing the precipitate and paper thoroughly with dilute ammonia water, catching the filtrate in a 200-ml electrolytic beaker. Neutralize with 1:1 sulfuric acid and add 10 ml excess. The

copper is obtained electrolytically as described above, using platinum electrodes, with a rapidly rotating anode and with a current of 1.0 anamp. Zinc is determined as described above.

Standardize the potassium ferrocyanide solution, using high purity zinc oxide. Ignite about 2 g of zinc oxide in a porcelain crucible for 20 min and cool in a desiccator. Weigh out accurately samples of about 0.2 g, cover with 20 ml of water, and add 6 ml of concentrated sulfuric acid. When dissolution is complete, dilute to 200 ml and titrate.

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Cadmium

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The main purpose of cadmium plating is to provide a corrosion-protective coating with an attractive appearance on various basis metals, especially on iron and steel, but also on copper and copper-rich alloys and on other metals and alloys.

On account of the relatively high price of cadmium, it is applied largely where thin coatings suffice, i.e., on parts which are used indoors or in sheltered positions outdoors. However, aircraft, marine, and military outdoor uses are common.

Cadmium plating is seldom used as an undercoating for other metals. Thin silver coatings are adsorbed by the cadmium, causing the surface to turn gray. No advantage is seen in using cadmium as an undercoating for nickel. Since cadmium covers cast and malleable iron better than zinc from a cyanide bath, it finds use as an undercoating, up to 0.0001 in. thick, for zinc.

The resistance of cadmium plate to chemicals is generally quite low. Cadmium plating is often used on parts or on assemblies consisting of dissimilar metals, such as steel and brass, to minimize voltaic couple corrosion. The electrical industry makes use of cadmium plate on steel and other metals because it is easily soldered to¹ and has low contact resistance.^{2,3}

Although formulas for cadmium cyanide solutions were published as early as 1849,⁴ cadmium plating was not used commercially before 1915. Mathers and Marble⁵ published the first comprehensive article on the subject and included an excellent survey of the early literature.

Commercial cadmium plating received its first impetus through the work of Udy in 1919.⁶ His solution was prepared from cadmium hydroxide and contained sodium cadmicyanide and sodium hydroxide

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but no free sodium cyanide. Udy recognized the need for baking of cadmium-plated, high carbon steel parts to eliminate hydrogen embrittlement.

Humphries⁷ introduced the first brightening agent, a caustic solution of wool or other proteins, into cadmium cyanide solutions in 1922. Hoff⁸ presented a detailed discussion of the properties of cadmium plate and cadmium plating solutions in 1926.

Subsequent developments have been confined largely to cyanide solutions and have been directed along four major lines. New brightening agents for the cyanide solutions have been found which provide a wider bright plate range. Increased and more uniform luster is obtained on recessed articles by the use of bright dips. Detailed studies of anode conditions during dissolution have led to new anode designs and construction. An understanding of the functions of the bath constituents and of the effect of foreign materials in the bath, notably metallic impurities and oxidizing agents, has led to improved bath formulas and better control of plating conditions. Carefully conducted exposure tests, outdoors and indoors, under controlled conditions have confirmed the cathodic protection to steel afforded by cadmium coatings and have more clearly defined their usefulness.

The only acid cadmium plating baths of commercial importance are the sulfate baths. They are used for the electrowinning of cadmium at Great Falls, at Trail, at Rislton, and elsewhere.^{9, 10} General information about the acid sulfate and other acid cadmium solutions may be found in several references.¹¹⁻¹⁴ Low pH cadmium sulfate solutions may be used to provide very thin but highly adherent under-coatings for heavy coatings from cyanide cadmium baths.¹⁵

Other baths recently proposed include the polyamine (such as ethylenediamine) bath¹⁶ operated at pH 10 and the fluoborate bath.¹⁷

PRINCIPLES

Almost every plating bath characteristic of consequence is in favor of the cyanide cadmium bath: its ability to give a dense, fine-grained deposit which may be made highly lustrous and reflective by the use of brighteners that are stable in the bath; high and easily balanced anode and cathode efficiencies; excellent covering power and good plate distribution on recessed articles. Consequently the cyanide bath is used almost exclusively for commercial cadmium plating, and no other bath will be discussed here.

BATH COMPOSITION AND FUNCTION OF CONSTITUENTS

Commercial cadmium baths consist essentially of sodium cadmium cyanide, sodium cyanide, and sodium hydroxide, plus organic and sometimes inorganic addition agents and brighteners.^{18,19} They are usually made by dissolving cadmium oxide in sodium cyanide solution, which automatically results in a bath with a sodium hydroxide content equivalent to the cadmium content. Thus, for each ounce per gallon of cadmium, there is originally present about 0.094 oz/gal of sodium hydroxide.

The composition of the cyanide complex is not known with certainty. Soderberg¹⁹ concludes that for practical purposes it may be $\text{Na}_2\text{Cd}(\text{CN})_4$, and considers the sodium cyanide used in excess of this formula to be free sodium cyanide, effective in dissolving the anodes. A bath may be operated on the basis of the cadmium metal and the free or total sodium cyanide concentrations as determined by analysis, but the free cyanide determination is likely to give too high results; hence the total cyanide method is more reliable.

The following formulas cover the typical cadmium plating baths in current use:

	Still Plating		Barrel Plating	
	oz/gal	g/l	oz/gal	g/l
CdO	3-5.2	23-39	2.7-4.5	20-32
Cd metal	2.5-4.5	19-34	2.3-3.8	17-28
NaCN	11.5-17.5	86-131	8.8-15	66-110
Addition agents				

As usual in plating baths, the cathode current density range for best results widens and moves toward higher current densities as the cadmium content increases. The choice of cadmium concentration depends largely on the relative value of the investment in tank, solution, and floor space, which decreases with increasing metal content, and the cost of drag-out, which increases with the metal content. Barrel plating solutions ordinarily are operated with rather low cadmium metal content, because of the agitation employed, whereas still tank and automatic solutions are operated over the whole range indicated in the formulas above. Much higher cadmium concentrations have been used for deposition of heavy coatings, whereas lower concentrations favor coverage in very low current density areas.

The sodium cyanide content is important in that it provides conductivity and makes anode corrosion possible. For these reasons a relatively constant free sodium cyanide content of 8 and 10 oz/gal is fre-

quently maintained in still tanks and barrels respectively. In some baths the appearance of the plate depends on the ratio between total sodium cyanide content and cadmium metal content ($R = \text{NaCN}/\text{Cd}$), and this ratio is controlled at $R = 3.75 \pm 0.4$.

The caustic soda content is usually considered not very critical. Except where there is much drag-in of pickling acid through insufficient rinsing, it is maintained automatically by the difference in anode and cathode efficiencies. Its prime function is to provide conductivity, which is of particular value for maximum output of a barrel. However, it should not be added much in excess of what is formed originally, since an excess causes a narrowing of the bright plate current density range. The effect of $p\text{H}$ of a low metal bath without brightener and a high metal bath with brightener on plating range has been determined.²⁰

The organic brighteners used in cyanide cadmium plating solutions include complex nitrogen-containing condensation products of high molecular weight,²¹⁻²⁵ piperonal with aluminum,²⁶ and certain sulfonic acids.^{18,27} Many other substances used as brighteners have been patented, most of which are effective in baths of relatively low concentration.²⁸⁻³¹ As the bath concentration and cathode current density are increased, it becomes progressively more difficult to secure smooth bright deposits by the use of organic addition agents alone; then addition of small amounts of certain metallic salts may be used to secure optimum results. Nickel and cobalt salts,^{18,34} when employed in conjunction with suitable organic addition agents, permit the use of current densities considerably in excess of those obtainable with the organic addition agents alone. Nickel tends to codeposit with cadmium to a very slight extent when the bath composition becomes low in cadmium or sodium hydroxide. Cobalt is equally as effective as nickel, but is required in larger amounts and does not codeposit with cadmium under conditions observed in normal bath operation.

OPERATING CONDITIONS AND CHARACTERISTICS

CURRENT DENSITY

The cathode current density range of the cadmium plating bath varies widely with the bath composition, temperature, and agitation and, under commercial conditions, ranges between 5 and 50 amp/sq ft. Thus the average effective current density is 15 to 20 amp/sq ft in

solutions containing 2.5 oz/gal of cadmium, and 30 to 40 amp/sq ft in baths with 5 oz/gal of cadmium. The anode current density under commercial plating conditions should be not over 20 amp/sq ft for effective anode corrosion and solution composition maintenance. The anode surface used naturally depends considerably on the required plate distribution.

TEMPERATURE

Cadmium plating is usually conducted at room temperature. In general, the bath temperature should be maintained between 20° and 35°C for uniform results, although considerable variation beyond these limits can be tolerated, particularly if suitable changes in bath composition are made to compensate for them.

CURRENT EFFICIENCY

The cathode current efficiency varies with bath composition and ranges between 85 and 98%. It is ordinarily between 90 and 95%. Generally speaking, the efficiency is increased with increased metal content, temperature, and agitation. Increased cyanide and brightener concentrations decrease the efficiency somewhat, and increased caustic soda content increases it slightly. The carbonate content of the bath has no appreciable effect on cathode current efficiency.

The anode current efficiency is usually close to 100% unless the anodes polarize as a result of too high current density or too low sodium cyanide concentration.

THROWING POWER

The throwing power and the covering power of the cadmium cyanide bath are high. The throwing power ranges between 40 and 45%, based on Haring cell measurements with a distance ratio of 5. A detailed study of a high metal bath³⁵ led to the conclusions that at a certain average current density throwing power is reduced as the temperature is raised, that at a given temperature throwing power increases with increased average current density, and that constant throwing power is maintained at rising temperature only by increasing the current density. High free cyanide and low metal contents favor throw.

The specific resistivity of the cadmium cyanide bath is low, approximately 5.6 ohm-cm.

MAINTENANCE AND CONTROL

Cadmium plating baths are easy to control under commercial conditions. Filtration is desirable to remove suspended matter which may cause rough deposits. However, the cadmium bath is not so susceptible to formation of rough deposits as, for example, nickel and copper baths; hence filtration is not considered necessary in many commercial installations.

Pitted cadmium deposits are seldom encountered. When pitting does occur, attention should first be directed to perfection of the cleaning of the basis metal. Anodic cleaning has been found particularly effective in eliminating pitting. Thallium in very small amounts, which may be introduced from the anodes, causes pitting at low current densities. Mild cases are relieved by additions of 0.001 to 0.05 g/l of sulfonated castor oil,³⁶ severe cases by removal of the thallium and the source of the contamination.

Cadmium plating baths are very susceptible to certain metallic impurities, which usually cause the plate to become discolored. The principal deleterious impurities from which the baths must be protected are thallium, lead, antimony, arsenic, tin, and silver.¹⁸ They can be removed by treating the baths with freshly precipitated cadmium sponge or zinc dust followed by filtration. Electrolysis at low current densities is also effective.

Cathodic depolarizers like nitrate and chromate ions seriously reduce the cathode efficiency.¹⁹ In a low metal bath 0.2144 oz/gal NO_3^- reduced it to 60% without visible effect, and 5.36 oz/gal NO_3^- to 30% with slight loss of brightness. Very small amounts of chromic acid (CrO_3) caused blistering, and 0.5, 1.0, and 1.9 g/l chromic acid prevented full coverage and lowered the efficiency from 95% to 85, 22, and 1% respectively.

Misplaced cadmium plate may be removed chemically by immersion in 1 lb/gal ammonium nitrate solution or anodically from steel either in a solution of 12 oz/gal sodium cyanide and 2 oz/gal caustic soda at room temperature and 6 v or less, or in an alkaline alkali metal pyrophosphate bath.³⁷

The practical control of a cadmium plating bath is relatively simple and is based on plating tests and solution analysis. The Hull cell³⁸ provides a convenient method for observing the plating characteristics over a wide range of current densities on one plate. Usually about one half of the maximum current density indicated by the Hull cell test is the maximum practicable current density.

SODIUM CARBONATE

Sodium carbonate tends to build up in the bath through decomposition of cyanide, which is accelerated by excessive bath temperatures and by absorption of carbon dioxide from the air. Since modern horizontal barrels draw as much as 4 amp/gal, they frequently require artificial cooling to prevent excessive carbonate formation. Small amounts of carbonate are not objectionable, but an excess should be removed for optimum operation of the bath. The concentration of sodium carbonate should not be allowed to exceed about 6 oz/gal in baths with 5 oz/gal of cadmium or 11 oz/gal in baths with 2.5 oz/gal of cadmium.

REMOVAL BY COOLING TO PRECIPITATE SODIUM CARBONATE

The carbonate can be brought down to about 3 oz/gal by subjecting the solution to a temperature of 0°C (e.g., in a tank placed out of doors during the cold months) or by immersing into it steel containers with naphtha to which solid carbon dioxide is added. Ordinarily 2.5 gal of naphtha and 100 lb of carbon dioxide are required per 100 gal of solution. During cooling the tank should be well covered and the carbon dioxide added at intervals over a period of 12 to 24 hr.* Cooling by the addition of crushed ice is less effective because of the melting of the ice and consequent dilution of the plating solution; this may lower the sodium carbonate content to 8 oz/gal. The sodium carbonate crystals are allowed to settle to the bottom of the tank, and the supernatant liquid is removed as quickly as possible by pumping or siphoning. Finally, the crystals are placed on a sheet of muslin stretched over a container to drain. It is sometimes necessary to seed the cooled solution with crystals of sodium carbonate in order to start the crystallization. The loss of cadmium and cyanide is practically nil if the freezing temperature is kept above -1°C.

REMOVAL BY PRECIPITATING AN INSOLUBLE CARBONATE

The sodium carbonate may also be converted to an insoluble carbonate and removed by filtration; calcium sulfate is commonly used for this purpose.³⁹ The calcium carbonate precipitate is removed by filtration. Since this is rather bulky, filtration may be slow if the capacity of the filter is small relative to the volume of the solution and the sodium carbonate content of the bath. Hence part of the carbonate may be removed by freezing before the remainder is precipitated as calcium carbonate. The $\text{SO}_4^{=}$ introduced causes no sub-

stantial anodic attack on steel tanks or anodes as long as the hydroxide content of the bath is maintained.

ANALYTICAL METHODS

Standard analytical procedures are applicable to the analysis of cadmium plating baths where the facilities of a chemical laboratory are available. Rapid shop control methods have been devised and are obtainable through the purveyors of the cadmium plating processes on the market.

DETERMINATION OF CADMIUM

Cadmium is best determined by an electrolytic method: 5 ml of the plating solution is placed in an electrolytic beaker, diluted to 80 ml with distilled water, and electrolyzed with a standard rotating platinum gauze cathode and a platinum wire anode at 1.5 amp for 2 hr.

$$\text{g/1 Cd} = 200 \times \text{g Cd deposited}$$

$$\text{oz/gal Cd} = 26.8 \text{ g Cd deposited}$$

According to Hoff⁴⁰ the addition of an excess of ammonia under controlled conditions prevents the codeposition of any zinc present.

Volumetric Method for Cadmium. The cadmium content may also be determined by titration, although the method does not eliminate zinc and will be in error if this element is present. The method is as follows: 5 ml of t¹ plating solution is pipetted into a 400-ml beaker, diluted with 50 ml of distilled water, and warmed. Ten milliliters of a solution containing 150 g/l sodium sulfide is added with stirring. The cadmium sulfide precipitate is allowed to settle, then is put on a filter and washed with hot water containing a few drops of sodium sulfide solution. The precipitate, with the filter paper, is returned to the beaker and dissolved by boiling with 25 ml of concentrated hydrochloric acid and 25 ml of distilled water. The resultant solution is diluted with 200 ml of distilled water, neutralized with ammonia until red litmus turns blue, and acidified by adding concentrated hydrochloric acid until the litmus paper turns red again and 3 ml in excess. The solution is heated to near boiling and titrated with a standard potassium ferrocyanide solution using a 50-g/l uranyl acetate solution as an outside indicator, until a drop of the solution added to a drop of the indicator on a spot plate turns brown. The potassium ferrocyanide solution is made by dissolving 22 g of the crystallized salt in distilled water to make 1 l, and standardized against a solution pre-

pared by dissolving exactly 0.25 g of metallic cadmium in 5 ml of concentrated hydrochloric acid and 5 ml of distilled water, adding 150 ml of distilled water, heating to near boiling, and adding 10 g ammonium chloride just before it is titrated.

$$\text{g/l Cd} = 50 \times \begin{array}{l} \text{ml ferrocyanide used in titration} \\ \text{ml ferrocyanide used in standardization} \end{array}$$

$$\text{oz/gal Cd} = 6.67 \times \begin{array}{l} \text{ml ferrocyanide used in titration} \\ \text{ml ferrocyanide used in standardization} \end{array}$$

TOTAL SODIUM CYANIDE

Total sodium cyanide is best determined by a modified Volhard titration * according to the following procedure: Dilute exactly 1.0 ml of plating bath to about 50 ml. Add 5 g of a dry powdered mixture of 95% by weight NaHCO_3 and 5% by weight $\text{K}_2\text{Cr}_2\text{O}_7$ and dissolve. Titrate with a silver nitrate solution containing exactly 26.0 g/l silver nitrate and concentrated nitric acid, stirring constantly, to first permanent opalescence. The total sodium cyanide content is calculated as follows:

$$\text{g/l NaCN} = 15 \times \text{ml of standard AgNO}_3 \text{ solution used}$$

$$\text{oz/gal NaCN} = 2 \times \text{ml of standard AgNO}_3 \text{ solution used}$$

FREE CYANIDE

The free cyanide content is obtained by diluting a 2-ml sample with distilled water to about 100 ml, adding 2 to 5 ml potassium iodide solution (100 g/l), and titrating with a standard silver nitrate solution until permanent turbidity. One milliliter of 0.1 N silver nitrate solution equals 4.9 g/l free sodium cyanide.

SODIUM HYDROXIDE

The sodium hydroxide content can be determined by titrating a diluted sample with standard acid using sulfo-orange indicator.

SODIUM CARBONATE

The sodium carbonate content is determined as follows: Dilute 5 ml of the plating solution to 100 ml with distilled water in an Erlenmeyer flask, and warm. Add sufficient barium chloride solution (100 g/l) until no more precipitate is formed. Allow the precipitate to settle,

* High results are obtained in the presence of ferrocyanides which are precipitated as silver ferrocyanide, $\text{Ag}_4\text{Fe}(\text{CN})_6$.

take it on a filter, and wash with hot water; then bring it back into the flask with the filter paper. Add 50 ml of distilled water and a few drops of a 0.2% methyl orange indicator solution. From a burette add 1.0 N standard hydrochloric acid until the color changes to a permanent pink.

$$\text{g/l Na}_2\text{CO}_3 = 10.6 \times \text{ml standard acid used} \times \text{its normality}$$

$$\text{oz/gal Na}_2\text{CO}_3 = 1.42 \times \text{ml standard acid used} \times \text{its normality}$$

ANODES

Both soluble cadmium anodes and insoluble steel anodes are used in plating from cadmium cyanide solutions. The cadmium anodes are almost always chill cast and meet the following specification:⁴¹ cadmium, min., 99.9%; silver + lead + tin, max., 0.05%; arsenic + antimony + thallium, max., 0.005%.

Anodes made from bearing scrap generally contain too much silver and tin and frequently harmful amounts of nickel and lead. These impurities go into solution at high anode current densities and cause irregularities at the cathode, as previously mentioned. Or the impurities may form sludges at low current densities which will contaminate the plate and cause rough deposits. (Low anode current densities may produce a cadmium sludge.)

The current density versus anode polarization curves for cadmium in cadmium cyanide plating solutions have the same general shape as those of other soluble anodes.⁴² At first the polarization increases rather slowly with the current density to about 0.2 to 0.3 v, the anode maintaining a normal gray metallic color. Then, with only a very slight increase in current density, the polarization increases very rapidly to about 2.6 to 3.2 v. In this voltage range the anode is powdery black or burnished bright and some oxygen evolution is noticed. As the current density is increased still further, the anode becomes coated over with a white salt which may become rather thick, and then copious amounts of oxygen are evolved. The anode is now an oxygen electrode, and the polarization then increases only slowly with increasing anode current density. Since under normal conditions it is desirable that the anodes dissolve with 100% efficiency to make up for the metal plated out and lost by drag-out, the anodes should have a gray metallic appearance. A visual inspection of the anodes will reveal whether or not the anode area or the cyanide content is too low.

Close control of the anode current density, to keep it below the limiting value at which the oxygen begins to evolve and the cadmium

anodes become less than 100% efficient, is particularly important when anodes are designed for plating the inside of tubes or other deep recesses. Since such anodes have an area which frequently is much smaller than the cathode area, a choice has to be made between using soluble cadmium anodes at low cathode current density (slow plating) or insoluble steel anodes.

The limiting anode current density varies primarily with the free sodium cyanide content of the bath (defined as the excess present above that required by the formula $\text{Na}_2\text{Cd}(\text{CN})_4$) and its carbonate content. An increase in the free cyanide content from 2 to 10 oz/gal in a solution containing 2.6 oz/gal of cadmium and 1.9 oz/gal of sodium hydroxide will increase the limiting anode current density from 20 to 30 amp/sq ft.⁴²

An increase in the sodium carbonate content from 0 to 20 oz/gal in a solution containing 2.6 oz/gal of cadmium, 1.9 oz/gal of sodium hydroxide, and 8 oz/gal of free sodium cyanide decreases the limiting anode current density from 30 to 20 amp/sq ft.⁴²

Strong oxidizing agents such as sodium chromate (formed when chromic acid accidentally enters the solution) or nitric acid or nitrates cause severe anode polarization, even if only very small amounts are present.

The oxygen overvoltage on steel is high,¹⁹ namely 0.49 v at 0.051 amp/sq ft and 1.95 v at 5.1 amp/sq ft, as measured against a non-polarized cadmium electrode in solutions containing 2.6 oz/gal of cadmium and 2 to 10 oz/gal of free sodium cyanide, the results being practically independent of the free sodium cyanide content. Because at a given current density the oxygen overvoltage is much higher than the potential of a dissolving cadmium anode, the simultaneous use of soluble and insoluble anodes generally requires that the individual anode voltages be controlled by means of separate rheostats.

Since the oxygen overvoltage is higher on a completely polarized cadmium anode than on steel, namely about 3 v against a maximum of about 2 v, a cadmium anode cannot become completely inactive as long as there is a steel anode in parallel. This fortunate condition, which prevails in all cyanide baths, makes possible anode designs and construction like the ball anode⁴³⁻⁴⁵ and the use of anodically charged steel parts on plating barrel cylinders.⁴⁶ As a matter of fact, except for this high oxygen overvoltage on steel, plain steel tanks could not be used for cyanide plating solutions, as otherwise stray currents would attain unmanageable magnitudes.⁴⁷ The presence of chloride ions in the bath should be avoided because they cause attack on nor-

mally insoluble steel parts when anodically charged by intent or by accidental intermediate electrode effect. Contamination of the bath by chloride may be brought about by the use of heat-treating cyanide mixtures instead of plating cyanide, by drag-in of pickling acids via contaminated rinse water, or by drag-in of decomposable chlorinated organic solvents.

When considerable current passes through anodic steel, its surface becomes oxidized, and a coating, apparently of rust, appears. This coating interferes with the current flow, increasing the voltage necessary for a given current density. The coating must be removed at intervals from steel anodes. There are indications that steel anodes used alone cause oxidation of cyanide to carbonate.¹²

PREPARATION OF BASIS METALS

Practically all cadmium plating is being done on the rough or machined basis metal without any polishing or buffing treatment. Small parts are sometimes ball-burnished prior to plating.

The standard plating cycle includes alkaline cleaner, warm rinse, cold rinse, acid pickle, cold rinse, cadmium plate, cold rinse, hot rinse, and drying.

Cleaning in organic solvents, to remove heavy oil and grease, may precede the alkaline cleaning. Steel parts are frequently precleaned by immersion without current in a cleaner with a high content of caustic soda and soap. On barrel work such a cleaner is used alone with tumbling or other agitation. Racked work is ordinarily electro-cleaned. Especially satisfactory results are obtained when steel is cleaned anodically in properly compounded cleaners.

Pickling of steel is ordinarily done at room temperature in hydrochloric acid (10 to 75% by volume of 18°Bé acid). Heavy scale is best removed in sulfuric acid (5 to 10% by volume of 66°Bé acid) at 66° to 77°C. If inhibitors are used to lessen the attack on the steel, the work should be given a short dip in uninhibited muriatic acid before proceeding. Steel forgings, and especially cast iron, are frequently cleaned by sand or shot blasting. Scale on copper and red brass is commonly removed in hot dilute sulfuric acid, scale on yellow brass in a cold dilute sulfuric acid. Brass and copper are then usually bright-dipped in a solution of sulfuric, nitric, and hydrochloric acids.¹³

Wernick¹⁴ has shown that an undercoating of tin from a stannate bath greatly improves the resistance of cadmium to intermittent 10% sodium chloride salt spray.

Aluminum, and presumably magnesium, that has been zinc coated by immersion (see Chapter 13) can be cadmium-plated if first struck in a solution containing 2 oz/gal cadmium and 7.5 oz/gal sodium cyanide.⁵⁰

POST-PLATING TREATMENTS

BRIGHT DIPS

Cadmium coatings are generally used "as plated." The most common method of finishing is known as bright dipping. The known bright dips are acid solutions of considerable oxidizing power. The cadmium plate dissolves without hydrogen evolution apparently in the same manner as a semi-polarized cadmium anode at a potential sufficiently high to prevent preferential etching of the crystal faces. The bright dips may contain single compounds such as $\frac{1}{2}$ to 1% by volume of concentrated nitric acid⁵¹ (of sp. gr. 1.4) or bromic acid,⁵² or they may be mixtures of acids with suitable oxidizing agents such as chromic acid^{53, 54} and hydrogen peroxide.^{55, 56} Typical compositions are 13.3 oz/gal of chromic acid with 0.14 fl oz/gal of concentrated sulfuric acid (sp. gr. 1.84), and 7% by volume of 30% (100-volume) hydrogen peroxide with 0.3% by volume of concentrated sulfuric acid (sp. gr. 1.84). The time of immersion in the bright dips is usually from 2 to 30 sec, depending on their concentration.

The chromic acid bright dip is characterized by the high degree of passivity which it imparts to the cadmium. Hence its judicious use does not reduce the corrosion protection to steel afforded by the cadmium plate.⁵⁷ The nitric acid bright dip has the disadvantage that it tends to discolor a cadmium surface when the articles are subsequently stored in a small, confined space.⁵⁸ The acidified hydrogen peroxide dip has the advantages of being free-rinsing and not producing any stains or other aftereffects.

ANODIC BRIGHTENING

The anodic brightening of cadmium in a cyanide bath has been proposed for treatment of dull cadmium deposits.⁵⁸⁻⁶⁰

MECHANICAL FINISHING

Mechanical finishing of cadmium plate is used only to a small extent. Such finishing necessitates sufficient care in the preparation of the basis metal before finishing that good adhesion is assured and

blistering prevented. Large cadmium-plated metal parts may be buffed or scratch-brushed with light pressure. Buffing is usually done with an unstitched buff having a surface speed of 2000 to 4000 ft/min. The work may be dry or wet. Small parts are ball-burnished at an average speed of rotation of 35 rpm, the volume of highly finished steel balls being at least twice that of the work. The work is covered with water, and a handful of neutral burnishing soap and 1 to 2 oz of sodium cyanide are added to a burnishing barrel of ordinary size.

LACQUERING OR PAINTING

Cadmium plate is sometimes finished by lacquering or painting. Many clear lacquers, including "water-dip" lacquers, are available which adhere well to cadmium as long as ordinary precautions of cleanliness are taken. Pigmented lacquers, "lacquer enamels," and paints frequently do not adhere very well. They require a pretreatment of the plate, preferably by phosphatizing⁶¹ in a suitable bath.⁶² Treatment in cold chromate solutions, such as 4 to 7 oz/gal chromic acid, for 1 to 2 min,⁶³ or in 6.5 oz/gal chromic acid with 0.7 oz/gal (0.3% by volume) of sulfuric acid (sp. gr. 1.84) for 5 to 10 sec^{64, 65} has also been used.

COLORING

Coloring of cadmium plate is not very common, and most solutions proposed for coloring are not very suitable. There are several proprietary solutions of the protective-chromate type that also color the cadmium. Yellows through orange through greens to black are produced in dichromate solutions containing alkali iodate, bromide, thio-cyanate, thiosulfate, or sulfonic acid,⁶⁶ and in chromic acid, chromate, or dichromate solutions containing zinc chloride.⁶⁷ Other colors, including blues and reds, are said to be obtained by first coating the plate in a chromic acid or chromate solution containing formic acid and, after rinsing, dyeing it in a water solution of a suitable dye.⁶⁸ Yellow to deep brown shades are produced in a solution containing 1 oz/gal potassium dichromate with 0.5 oz/gal nitric acid (sp. gr. 1.33).⁶⁹ This solution is kept at 60° to 70°C, and the dry parts are immersed in it for a few seconds to 8 min; they are then rinsed and dried. Immersion for 10 to 15 sec in a solution containing 1.4 oz/gal antimony chloride and 20% by volume of hydrochloric acid (sp. gr. 1.14), rinsing, wet pumice scrubbing, rinsing, and drying give an effect rather similar to a French gray finish.

HEATING

To eliminate hydrogen embrittlement of high carbon steel, the plated parts should be heated for 1 to 3 hr in an even temperature oven at 135° to 214°C. Steel, especially spring steel, that was nearly saturated with hydrogen prior to plating in its manufacture or during pickling, is likely to crack during plating and cannot then be restored by any treatment. Where this does not happen, cadmium plate is superior on springs to zinc or tin plate.⁷⁰

TESTS OF DEPOSITS

Extensive outdoor exposure tests have been conducted jointly by the Bureau of Standards, the American Electroplaters' Society, and the American Society for Testing Materials.⁷¹ The protective value is roughly proportional to the minimum thickness of the coating. The actual rate of penetration varies greatly with the corrosiveness of the atmosphere and the manner in which the parts are exposed. The effect of rain⁷² and of high relative humidity⁷³ in causing progressive corrosion has also been studied. For a summary of these and a variety of other corrosion tests the reader is referred to the chapter on cadmium coatings by Soderberg in *Corrosion Handbook*.⁷⁴

Specifications of the American Society for Testing Materials for "Electrodeposited Coatings of Cadmium on Steel"⁷⁵ call for three types of coatings, with minimum thicknesses on significant surfaces of 0.0005, 0.0003, and 0.00015 in (0.0125, 0.0075, and 0.0038 mm) respectively, of uniform appearance, bright or dull as specified, adherent, and free from blisters. The thinnest coating is commonly used for indoor exposure when an atmosphere of ordinary humidity and corrosiveness is encountered. The heavier coatings are used for outdoor exposure in shielded positions or in less corrosive atmosphere.

The standard method for testing for minimum thickness of cadmium deposits is the linear, microscopic method,⁷⁶ which, however, requires not only expensive equipment but also extensive experience for accurate interpretation of the results. Other more rapid but somewhat less accurate methods have been proposed, of which the dropping test is one of the simplest and most widely used. The original method of Clarke⁷⁷ used a solution of iodine in potassium iodide. The best solution for the purpose is that proposed by Brenner⁷⁸ containing 27 oz/gal chromic acid and 6.7 oz/gal sulfuric acid, which produces quite sharp endpoints and is insensitive to impurities in the plate. This

solution is dropped at a rate of 100 ± 10 drops per minute on the cadmium-plated surface until the appearance of the basis metal. The stripping rate depends on the temperature as follows:

Temperature	Rate of Penetration per 10 Sec
21°C (70°F)	0.000133 in. (0.0033 mm)
28°C (82°F)	0.000146 in. (0.0037 mm)
35°C (95°F)	0.00016 in. (0.0040 mm)

In general, an accuracy of about 15% is obtained in the dropping test.

A promising method, described by Francis,⁷⁹ consists in dissolving the plate anodically in a 10% solution of sodium cyanide in a small tube held against the surface. The thickness is calculated from the known current density (at which 100% anode efficiency is obtained) and the time which elapses before the cell voltage changes rather sharply.

In a time-of-gassing test proposed by Clarke and Andrew⁸⁰ the part is immersed in concentrated hydrochloric acid (sp. gr. 1.16) containing 10% $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. The thickness is read from a curve with an accuracy of about $\pm 25\%$, which is much better than that obtained with the much more impurity-sensitive antimony chloride-hydrochloric acid test now discarded.

A test widely used for small, especially threaded parts was developed by Soderberg.⁸¹ The part is immersed during successive equal time periods, the length of which depends on the temperature, in a solution of 25 g/l of chromic acid and 35 ml/l of concentrated nitric acid, and between each immersion it is rinsed in 5% by volume of hydrochloric acid and then in water to remove the brown film. The number of dips before appearance of steel or, for old coatings on brass, a bright alloy layer, are counted. Each dip is equivalent to 0.00005 in. The time period per dip varies as follows:

Temperature	16	21	27	32	38
°C	16	21	27	32	38
°F	60	70	80	90	100
Time per dip, sec	14.8	14.0	12.9	11.6	10.0

If the undersurfaces of the articles are disregarded, the thickness at all points may be obtained with an accuracy of $\pm 15\%$.

The magnetic method is also used.⁸² The instrument is calibrated to read numerical values which are translated into thickness of deposit from a suitable curve. Results within 10% are obtained on smooth surfaces. The instrument is not very suitable for testing cadmium plate thicknesses on rough surfaces.

Porosity tests are of little practical importance because porosity affects corrosion protection but little. A test which has found some use in England⁸³ consists of immersion in 1% by volume hydrochloric acid at 20°C for 10 min and observation of hydrogen gas bubbles formed at discontinuities.

Stress in cadmium deposits is slightly compressive⁸⁴ and of apparently no practical importance.

6.

Chromium

THE CHROMIUM PLATING PROCESS

GEORGE DUBPERNELL*

Chromium plating is extensively employed as a final finishing operation on many articles in general use. It may be divided into two general categories. In the first, which is the most generally known, the chromium is deposited as a thin coating to serve as a non-tarnishing, durable surface finish for decorative purposes on metal articles. In the second category, in which chromium plating has found steadily increasing application, and which is usually referred to as industrial or "hard" chromium plating, heavy coatings are deposited so as to take advantage of the special properties of electrodeposits of this type. These include particularly their resistance to heat, low coefficient of friction, resistance to wear, and resistance to corrosion and erosion. In these industrial applications chromium is usually deposited directly on the basis metal without intermediate coatings of other metals.

The modern process of chromium plating resulted principally from the publicity given the work of Colin G. Fink, of Columbia University, beginning in 1924.¹ † Udy and Fink have each been credited with having independently discovered the basic principles.² Udy's work has not been published except in the trial proceedings of the suits on the Fink patents. Liebreich also made similar discoveries more or less simultaneously in Germany, but confused them by overemphasis on the supposed importance of the trivalent chromium also present in the chromic acid bath.³

HISTORICAL DATA

Probably the first to propose plating with chromium was Antoine César Becquerel (in 1843).⁴ He suggested the use of bivalent and

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† References for this portion of the chapter will be found on pages 170 to 177.

trivalent solutions, and that probably accounts for the fact that Junot's patents⁵ and Bunsen's investigations⁶ related to the use of such solutions.

The first to deposit chromium from chromic acid solutions appears to have been Geuther, in 1856.⁷ However, he was merely trying to disprove Faraday's law by electrolyzing chromic acid and other solutions. His claim was thought to be incorrect by Buff, who failed to obtain a chromium deposit.⁸ It was apparently not until about 1905 that Geuther was given credit for being the first to deposit chromium from chromic acid solutions, in connection with the work of Carveth and Curry⁹ in the laboratories of Bancroft at Cornell University. A paper on chromium deposition from bivalent and trivalent solutions was published by Carveth and Mott.¹⁰ Chromium deposition continued to receive attention in the Cornell laboratories. Sargent worked on it between 1909 and 1914, and Gillett mentions¹¹ steel pyrometer tubes plated for him by Sargent. However, Sargent's work was not published until 1920.¹²

Sargent's work indicated that chromium plating from chromic acid solutions should be practical, and stimulated a number of further investigations. Schwartz worked under Fink at Columbia University, and the publication of his paper¹³ created much further interest. This was climaxed by the discovery of the basic principles by Fink assisted by Eldridge; and by the independent discovery of these principles by Udy. On the Fink discoveries were based the inventions of U. S. patents 1,581,188 and 1,802,463, which led to the commercial introduction and development of the chromium plating process as it is known today.^{1,14}

The above is merely a sketchy outline of the history of chromium plating. Detailed accounts are given in various books, especially the publications of Schneidewind,¹⁵ Macchia,¹⁶ Dubpennell,¹⁷ Pfannerhauser,¹⁸ and Machu.¹⁹ Blum and Hogaboom²⁰ emphasize the effect of the introduction of chromium plating on other electroplating processes.

PRINCIPLES

Chromium cannot be deposited from a solution containing only chromic acid and water. There must be present in the bath, in addition to chromic acid, one or more acid radicals which act as catalysts to bring about or aid in the cathodic deposition of chromium. Those most commonly used are sulfates and fluorides, the latter frequently in the form of a complex fluoride such as fluosilicate (SiF_6^-). For successful continuous operation, the ratio (by weight) of chromic acid

to total catalyst acid radicals must be maintained within definite limits, and preferably at about 100:1 in the case of sulfate.

It is generally immaterial with what other substances the catalyst is combined when it enters the bath or from what sources it may be derived, but the material must be soluble. Some sulfate is present in all chromium plating baths, since it is contained in even the best grades of chromic acid commercially available. Sulfuric acid and sodium sulfate are the sulfate-bearing materials most widely used in the bath; fluosilicic acid is the fluoride-bearing material most commonly used. When referring to the amount of catalytic agent or acid radical in a bath, it is the total of such agents that is usually meant.

While the current efficiency in chromium plating baths is low (generally in the range of 10 to 20 per cent for bright plate), a fairly high rate of deposition is obtained owing to the relatively high current densities used. The voltages required are higher than in most other electroplating processes, and generally are in the range of 4 to 10 v, depending upon operating conditions. Consequently the generator capacity required for chromium plating is higher than that for most other metal plating, but this seeming disadvantage has not seriously hindered the widespread use of the process.

The relatively poor throwing power of chromium plating baths is a disadvantage. Nevertheless, remarkably good results are achieved, even in the plating of articles of irregular shape, if the optimum ratio of chromic acid to total catalyst acid radicals is carefully maintained. Special auxiliary anodes are sometimes used in order to cover deep hollows or recessed portions. Such auxiliary anodes are similar to those used in other types of plating and are designed in accordance with the well-known and long-established principles of ample size for current-carrying requirements and proper spacing for uniform distribution of current.

THEORY

As pointed out by Blum and Hogaboom,²⁰ no satisfactory theory of chromium plating from chromic acid baths has been proposed beyond the principles stated above. Why is it possible to deposit chromium from chromic acid solutions when small amounts of various anions are added? Why does the current efficiency vary so widely with the temperature, the current density, the concentration of chromic acid, and the proportion of catalyst anion added? Why do different anions give such widely different results according to their intrinsic properties? These are only a few of the questions which any satisfactory theory should answer.

The outstanding effort to answer these and other questions is perhaps that of E. Müller,²¹ who suggested the formation of an insoluble film of chromium chromate, $\text{Cr(OH)}\text{CrO}_4$, on the cathode. The results obtained under varying conditions are ascribed to effects of the conditions on such films. A film of this type is considered to prevent the deposition of chromium from pure chromic acid, and the deposition of chromium when sulfate or other anions are added is felt to result from modification of the film.

One of Müller's students, Ekwall, published²² the results of additional investigations. Ekwall concludes that the effect of sulfate in chromium plating is due to its greater tendency to form complexes with trivalent chromium than with chromate; thus it reacts with newly formed trivalent chromium and prevents the formation of basic chromic chromate at the cathode.

Another early investigator who worked extensively in this field was Liebreich.²³ Liebreich originally proposed that some chromic acid had to be reduced to the bivalent stage before chromium deposition could commence. He based his theories on very carefully made current-voltage curves, but these could not be reproduced by others. He later recognized the importance of catalyst anions, but continued to overemphasize the state of reduction of the solution or of the cathode film as a factor.

Kasper reviewed the theories proposed by others, and showed that basic chromium chromate is a colloid with an isoelectric point of about pH 6, while the cathode film is considered to have a pH of about 3 to 4.²⁴ He concluded that chromium is deposited directly from the hexavalent state, since metallic impurities such as copper prevent chromium deposition from chromous and chromic solutions, but not from chromic acid baths, and therefore chromous or chromic compounds produced in chromic acid baths are probably inactive. Kasper also described the effect of sulfate as due to its ability to coagulate basic chromium chromate and prevent its forming a film on the cathode which in turn prevents chromium deposition when no sulfate is present. Compare the theories of Müller and Ekwall described above.

Rogers made plating tests with widely varying concentrations of chromic acid, sulfate, and sodium hydroxide,²⁵ but made only a very few approximate measurements of the pH of the resulting solutions. From these tests he concluded that the pH of the cathode film was an important variable, and that chromium was deposited as a result of the reduction of chromous hydroxide formed on the cathode. This is similar to one phase of Liebreich's theories. Rogers' conclusions were questioned by Kasper²⁶ in the discussion to the Electrochemical Society

paper; this discussion is of interest for its clear statement of Kasper's views.

Snavely studied, by means of x-rays, the structure of chromium deposits formed under widely different conditions.²⁷ He considers that the deposition of chromium results from the deposition of hydrides of chromium, which decompose during plating and form the chromium deposit; this explains the shrinkage and cracking which generally occur during chromium deposition.

Kasper's concept that chromium is deposited directly from the hexavalent state has been confirmed by recent work at the National Bureau of Standards by Brenner and Ogburn.²⁸ These workers used radioactive chromium to show that chromium is deposited directly from the hexavalent state and not through an intermediate step involving trivalent chromium. Rogers and Burr²⁹ applied the theory of rate processes to the examination of data on the effect of sulfate, and reached the conclusion that the sulfate retards hydrogen deposition rather than catalyzing the plating reaction.

The theories proposed to date still do not seem to afford a fully satisfactory explanation for chromium deposition from chromic acid solutions. They offer little help to those desiring a qualitative understanding of the process, and it appears that further experimental work is necessary to establish a basis for a satisfactory theory.

FUNCTIONS OF CONSTITUENTS OF THE BATH

There are only two essential constituents in the conventional chromium plating baths: chromic acid, and one or more catalyst acid radicals.

Because chromium metal will not serve satisfactorily as anode, insoluble anodes are used, generally lead. The chromium to be deposited is introduced into the plating bath as a chemical, chromic anhydride, CrO₃, commonly called chromic acid. It is a reddish brown material, easily soluble in water. Many manufacturers, now aware of the effect of even small amounts of catalyst acid radicals, furnish a pure grade of chromic acid especially suited for chromium plating purposes. This chromic acid is made to meet specifications which require that it contain not more than a small fraction of a per cent of sulfate and be free from other catalysts.

A solution containing 53.3 oz/gal of chromic acid contains about 27.7 oz/gal of chromium. This is almost 2 lb of chromium in each gallon of solution, and, with complete utilization and no losses, it would be sufficient to cover about 4700 sq ft of surface with a deposit 0.00001

in. (0.25 μ) thick, the thickness commonly specified for decorative purposes.

To convert a pure chromic acid solution to a chromium plating bath a catalyst is necessary. With a given set of conditions of bath temperature, current density, and chromic acid concentration, too small an amount of catalyst will result in either no plate or in brown oxide stains. Too high a catalyst content will result in either partial plating with poor throwing power or none at all, owing to depolarizing action or easy formation of trivalent chromium at the cathode. The essential criterion of bath composition in chromium plating from the conventional chromic acid-sulfate radical solution is the ratio, by weight, of chromic acid to sulfate. This ratio should be kept within the limits of 50:1 and 250:1, and preferably at about 100:1.

Two typical formulas for chromium plating baths using sulfate as the catalyst acid radical are:

1. Chromic acid (CrO_3), 53 oz/gal (400 g/l); sulfate (SO_4^{2-}), 0.53 oz/gal (4 g/l).

2. Chromic acid (CrO_3), 33 oz/gal (250 g/l); sulfate (SO_4^{2-}), 0.33 oz/gal (2.5 g/l).

Formula 1 is frequently referred to as the "concentrated" bath, and formula 2 as the "dilute" bath. Although concentrations of chromic acid from about 7 oz/gal up to saturation (about 133 oz/gal) can be used, most commercial baths are operated between 33 oz/gal and 53 oz/gal. The important requirement is that the ratio by weight between the two constituents be maintained at about 100:1.

Baths containing 33 oz/gal of chromic acid have a slightly higher current efficiency than those containing 53 oz/gal. They also have a lower conductivity and, therefore, require a higher voltage for a given current density. The more dilute baths are also more sensitive to the addition or removal of catalyst acid radicals from drag-in and drag-out. Hence they require more frequent and more careful adjustment for maintenance purposes. For instance, if a small amount of sulfate from a sulfuric acid dip is dragged into a chromium plating bath operated at the lower chromic acid concentration, it will cause more change in the ratio than in a bath operated at the higher chromic acid concentration.

Fluosilicate has had considerable use as a catalyst in chromic acid baths. Such solutions are difficult to analyze and maintain. Whereas Bilfinger³⁰ has concluded that these baths are unstable and decompose, Gebauer³¹ found that they are stable even when subjected to a prolonged electrolysis of 47,500 amp-hr/gal on a laboratory scale, and 12,730 amp-hr/gal in a commercial bath of over 3000 gal capacity.

OPERATING CONDITIONS AND CHARACTERISTICS

With baths having compositions such as formulas 1 and 2, bright plate can be reliably obtained by properly coordinating temperature and current density within definite limits, taking into account in such coordination the chromic acid concentration of the bath. A convenient chart, showing the conditions for bright plating, is given in in

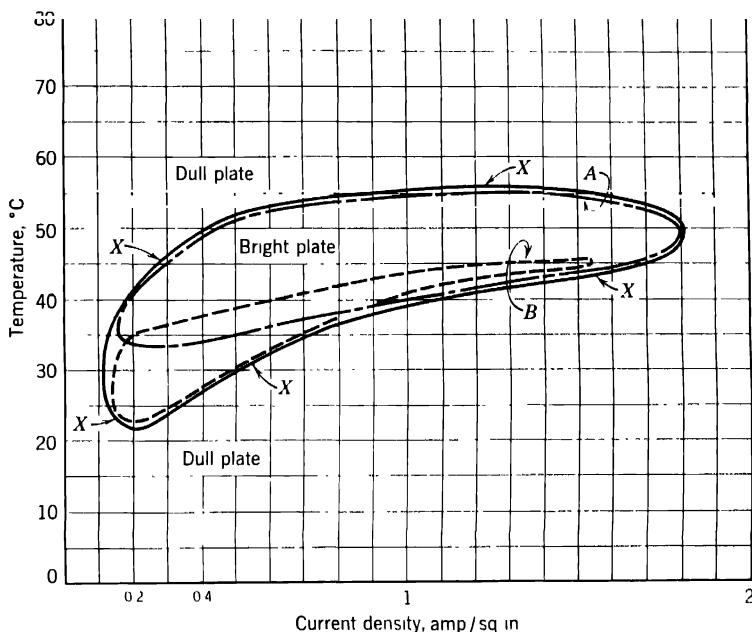


Fig. 1. Chart of bright plating conditions

Fig. 1, taken from U. S. patent 1,802,463.¹ In this figure the dot-and-dash line *A* circumscribes the bright plate area for solutions of formula 2, and the dash line *B* circumscribes a bright plate area for a solution similar to formula 1. The complete bright plate area circumscribed by the line *X* is typical of the behavior of most chromium plating baths. Thus, to produce bright deposits from formula 2 containing 33 oz/gal of chromic acid and 0.33 oz/gal of sulfate at a temperature of 40°C, cathode current densities as low as 29 amp/sq ft and as high as 144 amp/sq ft may be used, while at 45°C 50 per cent higher current densities may be used.

If more rapid plating is desired and sufficient power is available, the temperature is often increased to about 55°C and the current den-

sity to about 288 amp/sq ft or 2 amp/sq in. These conditions, when used with the dilute solution (formula 2) for building up a heavy plate for industrial purposes, result in a plating speed of almost 0.001 in. thickness of chromium per hour. Higher plating speeds can be obtained at higher current densities, but the deposits are apt to be "bubbly," "pebbly," or nodular.

Plating at higher temperatures and current densities has been proposed by numerous workers, among whom may be mentioned Willink,³² Brown et al.,³³ Wick,³⁴ and Blum.³⁵ This idea has been applied successfully to the plating of small articles, but the power required for plating larger objects may be prohibitive or unavailable.

Tables 1 and 2, on chromium plating speeds, and Table 3 on current efficiencies have been prepared from data obtained in United Chromium, Incorporated, laboratories.³⁶ A study was made of chromium deposition from solutions containing 33 oz/gal and 53 oz/gal, each with the ratio of chromic acid to sulfate radical of 100:1. The current efficiencies were determined under accurately maintained plating conditions in an apparatus so designed that the current was uniformly distributed over the entire cathode area plated.

Such accurate control of all plating conditions and such uniformity of current distribution are rarely obtained in production plating. In the shop it is frequently impractical to calculate the exact area of the work; it is difficult to estimate the proportion of the current taken by the rack or guard wires; slight variations in temperature and solution composition generally occur; and the ideal condition of uniform current distribution over a complicated piece of work can only be approximated. Hence one cannot expect the actual plating speeds in production plating to be absolutely identical with those given in the tables. However, the more closely the plating conditions approach the exact conditions represented by the figures in the tables, the more closely the resulting thicknesses of chromium plate will correspond to the thicknesses listed.

The plating speeds given in the tables have also been expressed graphically in Figs. 2 and 3, which may be used to supplement the tables, as they give interpolated values.

Table 3 gives current efficiencies for the 33 oz/gal chromic acid-sulfate solution and the 53 oz/gal solution (ratio 100:1) at various current densities and temperatures.

The current efficiency and, consequently, the plating speed were recently determined by Grube and Clifton³⁷ for solutions containing 10, 20, 30, and 40 oz/gal of chromic acid. The chromic acid-to-sulfate ratio was varied from 40:1 to over 300:1 at temperatures of 46, 55, and

TABLE I. CHROMIUM PLATING SPEEDS

Solution: CrO₃, 33.3 oz/gal (250 g/l); SO₄²⁻, 0.33 oz/gal (2.5 g/l).
Ratio, CrO₃:SO₄²⁻ = 100:1

Current Density, amp/sq in.	25°C (77°F)	35°C (95°F)	40°C (104°F)	45°C (113°F)	50°C (122°F)	55°C (131°F)	65°C (149°F)
	<i>Minutes per Thousandth</i>						
Time, in minutes, required to deposit 0.001 in. thickness of chromium							
0.25	1430	1410	1580	1760			
0.50	206	399	405	410	603		
0.75	107	201	205	208	271	520	
1.00	71	129	137	144	165	204	325
1.50	41	66	71	85	92	99	
2.00	28	42	48	59	63	64	90
2.50		29	36	45	47	50	
3.00	18	22	29	36	38	40	49
4.00		14	20	25	26	28	33
5.00			15	18	20	21	25
6.00					16	17	20
8.00				10	11	12	14
10.00						9	11
12.00							9
16.00							6

Thousands per Hour

Thickness of chromium, in thousandths of an inch, deposited
per hour of plating time

0.25	0.0119	0.0426	0.0380	0.0341			
0.50	0.291	0.150	0.148	0.146	0.0995		
0.75	0.560	0.298	0.293	0.288	0.222	0.115	
1.00	0.845	0.465	0.438	0.417	0.364	0.294	0.187
1.50	1.46	0.909	0.847	0.707	0.652	0.606	
2.00	2.14	1.43	1.24	1.02	0.953	0.938	0.667
2.50		2.07	1.65	1.33	1.28	1.20	
3.00	3.33	2.72	2.09	1.67	1.58	1.50	1.23
4.00		4.28	3.02	2.40	2.30	2.14	1.82
5.00			4.07	3.33	3.00	2.86	2.40
6.00					3.75	3.53	3.00
8.00				6.00	5.45	5.00	4.28
10.00						6.67	5.45
12.00							6.67
16.00							10.00

TABLE 2. CHROMIUM PLATING SPEEDS

Solution: CrO₃, 53.3 oz/gal (400 g/l); SO₄⁼, 0.53 oz/gal (4.0 g/l).
Ratio, CrO₃:SO₄⁼ = 100:1

Current Density, amp/sq in	Minutes per Thousandth						
	25°C (77°F)	35°C (95°F)	40°C (104°F)	45°C (113°F)	50°C (122°F)	55°C (131°F)	65°C (149°F)
Time, in minutes, to deposit 0.001 in. thickness of chromium ¹							
<i>Thousands per Hour</i>							
0.25	2110	1760					
0.50	212	543	594	603	846		
0.75	127	263	286	313	427		
1.00	88	153	176	205	264	325	
1.50	51	73	92	105	125	132	
2.00	35	45	59	68	77	86	151
2.50		30	43	50	55	62	
3.00	20	23	33	38	43	48	68
4.00		15	22	26	30	34	42
5.00			16	20	23	26	32
6.00					18	22	25
8.00				11	13	15	18
10.00						11	13
12.00							11

	Thickness of chromium, in thousandths of an inch deposited per hour of plating time					
	0.25	0.50	0.75	1.00	1.50	2.00
0.25	0.0284	0.0341				
0.50	0.283	0.110	0.101	0.0995	0.0709	
.75	0.472	0.228	0.210	0.192	0.140	
.00	0.682	0.390	0.340	0.292	0.227	0.185
.50	1.18	0.822	0.655	0.571	0.480	0.455
.00	1.71	1.33	1.02	0.882	0.779	0.697
.50		2.00	1.41	1.20	1.09	0.968
3.00	3.00	2.81	1.82	1.58	1.39	1.25
4.00		4.00	2.79	2.32	2.00	1.77
5.00			3.75	3.00	2.61	2.31
6.00					3.33	2.73
8.00				5.45	4.62	4.00
10.00						5.45
12.00						5.45

TABLE 3. CURRENT EFFICIENCIES, IN PER CENT OF THE ELECTROCHEMICAL EQUIVALENT FOR THE REDUCTION OF HEXAVALENT CHROMIUM TO METALLIC CHROMIUM

Current Density, amp/sq in.	25°C (77°F)	35°C (95°F)	40°C (104°F)	45°C (113°F)	50°C (122°F)	55°C (131°F)	65°C (149°F)
<i>Solution:</i> Average density, 21°Bé; CrO ₃ , 33 oz/gal (250 g/l); SO ₄ ⁻ , 0.33 oz/gal (2.5 g/l). Ratio, CrO ₃ :SO ₄ ⁻ = 100:1							
0.25	5.9	6.0	5.3	4.8			
0.50	20.3	10.5	10.4	10.3	7.0		
0.75	26.0	14.0	13.8	13.5	10.4	5.8	
1.00	29.3	16.4	15.4	14.7	12.8	10.4	6.5
1.50	33.9	21.2	19.9	16.6	15.4	14.2	
2.00	36.8	25.4	21.8	18.0	16.8	16.4	11.8
2.50		28.9	23.3	18.8	17.9	17.0	
3.00	39.1	31.8	24.5	19.6	18.8	17.5	14.3
4.00		36.4	26.6	21.2	20.1	19.1	15.9
5.00			28.6	22.5	21.0	19.7	17.0
6.00					22.0	20.6	17.8
8.00				26.0	23.9	21.9	18.5
10.00						23.0	19.4
12.00							20.3
16.00							22.0
<i>Solution:</i> Average density, 31°Bé; CrO ₃ , 53 oz/gal (400 g/l); SO ₄ ⁻ , 0.53 oz/gal (4.0 g/l). Ratio, CrO ₃ :SO ₄ ⁻ = 100:1							
0.25	4.0	4.8					
0.50	9.6	7.8	7.1	7.0	5.0		
0.75	21.9	10.7	9.8	9.0	6.6		
1.00	23.6	13.7	12.0	10.3	8.0	6.5	
1.50	26.9	19.4	15.3	13.4	11.3	10.7	
2.00	29.5	23.8	17.8	15.5	13.8	12.3	7.0
2.50		27.4	19.7	17.0	15.3	13.7	
3.00	33.8	30.6	21.2	18.3	16.2	14.8	10.3
4.00		35.3	24.4	20.1	17.4	15.4	12.5
5.00			26.3	21.5	18.3	16.0	13.4
6.00					19.2	16.4	13.9
8.00				25.0	21.0	17.9	14.8
10.00						18.5	15.9
12.00							16.4

63°C, and current densities of 100, 200, 300, and 400 amp/sq ft. The current efficiency was found to increase regularly as the concentration decreased down to 10 oz/gal of chromic acid. The average increase in efficiency on diluting the solution, with a ratio of 100:1, temperature 55°C and current density 288 amp/sq ft, was about 0.25 per cent per 1.3 oz/gal of chromic acid decrease in concentration. A

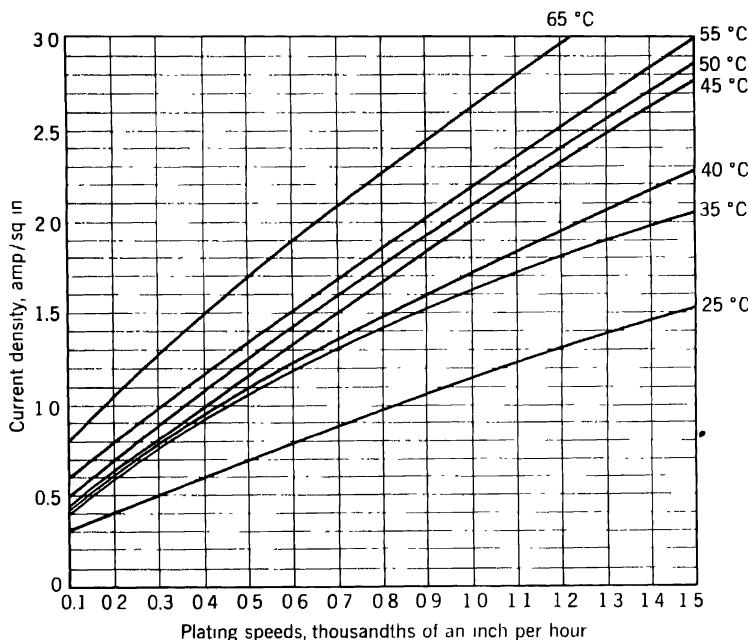


Fig. 2. Chromium plating speeds. Solution: 33 oz/gal CrO₃ (21°Bé); 0.33 oz/gal SO₄²⁻. Ratio, CrO₃:SO₄²⁻ = 100:1.

similar figure of about 0.27 per cent per 1.3 oz/gal of chromic acid can be calculated from Webersinn's data in Table 3 for chromic acid concentrations of 33 to 53 oz/gal, taking the data for 2 amp/sq in. (288 amp/sq ft) and 55°C. These figures are useful in calculating the plating speed variation with small changes in chromic acid concentration.

The effect of increasing sulfate content or decreasing ratio of chromic acid to sulfate from 100:1 down to 5:1 has been investigated by Bilfinger³⁸ for solutions containing 33 oz/gal of chromic acid. Although he worked only up to temperatures of 55°C and obtained low efficiencies at low ratios such as 10:1 and 5:1, Bilfinger suggests the use of higher temperatures and current densities, combined with

lower ratios of chromic acid to sulfate, to get higher plating speeds for hard chromium plating.

The acidity of chromium plating baths is very high. It is not ordinarily controlled or measured. What few measurements have been made (with the glass electrode) indicate values for acidity off the usual pH scale, and in the range of small, negative values of μH .³⁹

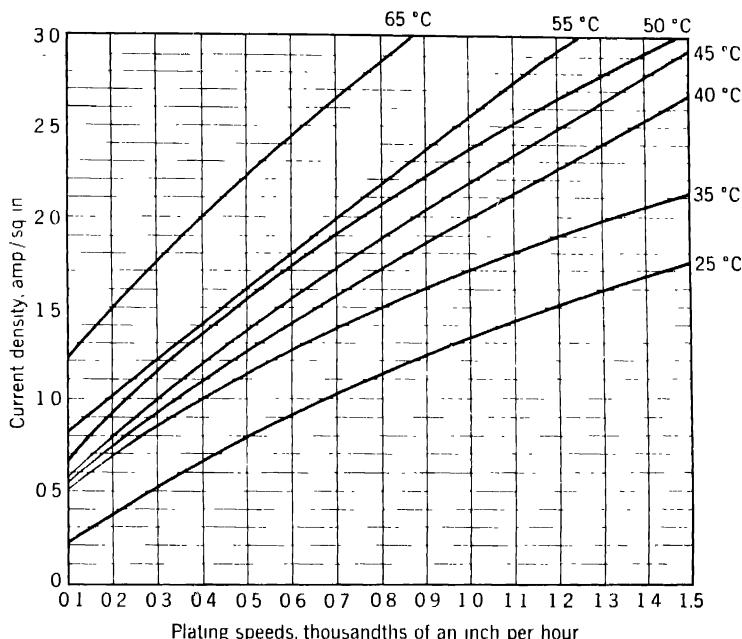


Fig. Chromium plating speeds. Solution, 53 oz/gal CrO_3 (31°Bé); 0.53 oz/gal SO_4^{2-} . Ratio, $\text{CrO}_3:\text{SO}_4^{2-} = 100:1$.

The throwing power of chromium plating baths is poor as compared with copper or nickel plating baths. The conductivity is high⁴⁰ but is reduced by such impurities as iron and copper. The cathode polarization during chromium deposition is relatively constant and substantially the same as that obtained during the electrolysis of the same concentration of pure chromic acid without chromium deposition. Therefore the major variables connected with throwing power in bright chromium plating are the current efficiency and the bright plating range. If a given set of conditions gives the widest possible bright plate range and the plating is done at an average cathode current density near the upper limit of current density for this bright plate range, the optimum throwing power will be attained.

In the conventional throwing power box, cyanide copper plating baths with good throwing power generally have a rating around 20 or 40 per cent, whereas most nickel plating and acid copper plating baths have a rating about zero, or relatively small positive or negative values. The throwing power in chromium plating has been found to vary from around -13 per cent under the best conditions to -100 per cent and even lower.⁴¹ More recent work is reviewed by an anonymous German author who gives thirty-six references.⁴² The throwing power on copper cathodes was investigated by Grube and Clifton.³⁷ A good discussion was given recently by Blum and Hogboom.²⁰

Cations which may be present in chromium plating baths are trivalent chromium, iron, copper, zinc, sodium, and others. Trivalent chromium usually results when baths are operated with too large a cathode area and too small an anode area, or when organic matter is introduced. The trivalent chromium content can be kept down by increasing the area of the anodes used, or, where this is not practical, by electrolyzing the solution for a period of time with a relatively large anode area and a small cathode area. Iron, copper, zinc, and other metallic impurities may be introduced into the bath in various ways; and, if permitted to accumulate, they cause an increase in the resistivity of the bath. None of the cations discussed has any beneficial effect on the operating characteristics of the bath. Trivalent chromium particularly is detrimental when present to the extent of more than a few grams per liter.

MAINTENANCE AND CONTROL

Chromium plating baths do not usually require filtering. If some clarification is desired, it can be accomplished by allowing the solution to stand overnight and then decanting or otherwise transferring the supernatant liquid to another tank. After the sludge remaining in the original container is cleaned out, the solution can be returned to it. If desired, a chromium solution may be filtered through a pad of glass wool or through fiber glass filter cloth. Filtering cloths of Vinylite (Vinyon) and Saran are also available and have substantially complete chromic acid resistance.

Chromium plating baths are very stable in use, and their composition can be readily maintained by physical or chemical analysis. Some of the chromic acid is reduced to trivalent chromium whenever chromium is being plated, but this trivalent chromium is continually re-oxidized to chromic acid on the lead peroxide surface of the lead

anodes commonly used. This automatically maintains the trivalent chromium concentration at a relatively low figure under usual operating conditions, especially if the area of the lead anodes is equal to or greater than the cathode area.¹³ If iron or other anodes are used for special purposes, they do not reoxidize the trivalent chromium to chromic acid as well as do lead anodes, and a higher equilibrium concentration of trivalent chromium is reached after the bath has been used for some time. Furthermore, these other anodes, unless completely insoluble, introduce contaminating metals such as iron into the solution, and therefore should generally be avoided.

Pitting is not commonly encountered in chromium plating baths, and no additions are made to influence the surface tension, nor is it necessary for control purposes to measure and adjust the surface tension of the bath. Wetting agents have been added recently to minimize the fumes evolved during chromium plating;¹⁴ the prospective user of such compounds should satisfy himself about their stability under his particular conditions.

Special physical measurements or plating tests are frequently made to check the condition of a bath or to determine the total catalytic effect of all the acid radicals present. Many plants use physical analysis instead of chemical analysis as the basis for making adjustments necessary for bath maintenance. Pinner and Baker¹⁵ proposed a bent cathode test to determine the ratio of chromic acid to total catalyst acid radicals. This was a modification of the strip test first used by Fink, described below.

Pfanhauer¹⁶ developed a so-called potentiometric method of checking the approximate catalyst content of chromium plating baths. This consists of an ammeter and voltmeter connected to a small plating cell with a 4- or 5-v source of direct current, and a rheostat. The solution to be tested is placed in the cell with lead anodes and a brass cathode. The applied voltage is slowly raised until there is a sudden increase in voltage and a deposit of chromium appears. The current density at which this occurs is noted, and the catalyst content of the bath in terms of sulfate is estimated from current-voltage reference curves plotted for solutions of known composition. A special instrument for making these measurements has been marketed in Germany for some time under the name "L. P. W. Sulfometer;"¹⁷ the ammeter of this instrument is calibrated to read the ratio directly.

Perhaps the most important plating test used with chromium plating baths is the determination of the current efficiency under known conditions, as first used by Fink as part of his strip test. When carefully carried out, this measurement gives a great deal of information

regarding the characteristics of a given bath and its total catalyst content. The appearance and distribution of the resultant plate under the test conditions can also be studied when data on current efficiency are being obtained. If the current efficiency is not required, the appearance of the plate at different current densities can be observed in a single measurement by means of a Hull cell.⁴⁸⁻⁵⁰

ANALYTICAL METHODS

DETERMINATION OF CHROMIUM IN CHROMIUM PLATING SOLUTIONS *

1. Pipette a 10-ml sample into a 500-ml volumetric flask, dilute to the mark, and mix thoroughly.
2. Pipette two 10-ml portions into two 250-ml Erlenmeyer flasks.
3. Dilute each with water to between 100 and 125 ml. Use one for A and one for B.

A. CHROMIC ACID DETERMINATION

1. Add 2 g ammonium bifluoride, NH_4HF_2 , to eliminate the effect of any iron present.
2. Add 15 ml HCl (conc. HCl, sp. gr. 1.18).
3. Add 10 ml KI solution (100 g/l KI + 1 g/l KOH).
4. Allow 0.1 N sodium thiosulfate solution (0.1 N $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) to run in from a burette until the brown color changes to straw color.
5. Add 3 ml starch solution (10 g/l soluble starch).
6. Continue titration until the blue color just disappears.
7. Calculate results:

$$(\text{ml } \text{Na}_2\text{S}_2\text{O}_3 \text{ used}) \times \text{CrO}_3 \text{ factor} = \text{g/l CrO}_3$$

(For 0.1000 N $\text{Na}_2\text{S}_2\text{O}_3$, CrO_3 factor is 16.67.)

Example.

$$\begin{aligned} \text{ml } \text{Na}_2\text{S}_2\text{O}_3 \text{ used} &= 23.8 & \text{CrO}_3 \text{ factor} &= 17.04 \\ 23.8 \times 17.04 &= 406 \text{ g/l CrO}_3 \end{aligned}$$

B. TRIVALENT CHROMIUM DETERMINATION

1. Add about 0.2 g Na_2O_2 .
2. Boil for 20 to 30 min.
3. Dilute to between 100 and 125 ml and allow to cool.

* Taken from United Chromium, Incorporated, Reference Sheet CA-5c

4. Add 2 g NH_4HF_2 .
5. Add 15 ml HCl (conc. HCl, sp. gr. 1.18) and allow to cool.
6. Add 10 ml KI solution (100 g/l KI + 1 g/l KOH).
7. Allow 0.1 N sodium thiosulfate solution (0.1 N $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) to run in from a burette until the brown color changes to straw color.
8. Add 3 ml starch solution (10 g/l soluble starch).
9. Continue titration until the blue color just disappears.
10. Calculate results:

(ml $\text{Na}_2\text{S}_2\text{O}_3$ used in B)

$$- (\text{ml } \text{Na}_2\text{S}_2\text{O}_3 \text{ used in A}) \times \text{Cr}^{+3} \text{ factor} = \text{g/l Cr}^{+3}$$

(For 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$, Cr^{+3} factor is 8.7.)

Example.

$$\text{ml } \text{Na}_2\text{S}_2\text{O}_3 \text{ used in B} = 24.6$$

$$\text{ml } \text{Na}_2\text{S}_2\text{O}_3 \text{ used in A (previous example)} = 23.8$$

$$\text{Cr}^{+3} \text{ factor} = 8.9$$

$$(24.6 - 23.8) \times 8.9 = 0.8 \times 8.9 = 7 \text{ g/l Cr}^{+3}$$

DETERMINATION OF SULFATE IN CHROMIUM PLATING SOLUTIONS *

1. Pipette a 10-ml sample into a 250-ml beaker.
2. Add 75 ml reducing mixture † and boil for 10 to 15 min.
3. Dilute with hot water to between 125 and 150 ml, and allow to stand in a constant temperature electric oven or water bath between 60° and 70°C for at least 1 hr, and overnight if convenient.
4. Filter into a 250-ml beaker, using a 12.5-cm Whatman No. 1 filter paper (or equivalent), and from 2- to 3-ml filter paper suspension; wash the green color from the filter paper with hot water.
5. Stir the filtrate, which should be between 175 and 200 ml, and heat to boiling.
6. Before allowing to cool below 70°C, add 10 ml barium chloride solution (100 g/l $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) from a burette drop by drop with stirring.

* Taken from United Chromium, Incorporated, Reference Sheet CA-2e.

† The reducing mixture is prepared by mixing together: 15 parts by volume, isopropanol, $(\text{CH}_3)_2\text{CHOH}$; 7 parts by volume, hydrochloric acid (conc. HCl, sp. gr. 1.18); 25 parts by volume, glacial acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$. The isopropanol (isopropyl alcohol), technical grade, has been found free from sulfate, is as effective as ethyl alcohol, and costs about one-eighth as much. The c.p. grades of hydrochloric acid and acetic acid are used. The mixture may be prepared in quantities and kept indefinitely.

7. Allow to stand in a constant temperature electric oven or water bath between 60° and 70°C not less than 2 hr and not more than 4 hr.

8. Filter at once, using 11-cm Whatman No. 42 filter paper (or equivalent) and from 2 to 3 ml ashless filter pulp suspension; wash thoroughly.

9. Transfer the paper and precipitate to a weighed 20-ml porcelain crucible; place in an electric muffle furnace and burn off slowly, finally holding at a bright red heat for about 15 min.

10. Cool in a desiccator, weigh the crucible, and calculate results:

$$\text{weight of precipitate in grams} \times 41.15 = \text{g/l sulfate}$$

Example.

$$\text{weight of precipitate} = 0.0973 \text{ g}$$

$$0.0973 \times 41.15 = 4.00 \text{ g/l sulfate}$$

The analytical control of chromium plating baths by methods such as those given above has been found the most dependable procedure. The specific gravity is a good indication of the chromic acid content with new baths, but may show considerable deviation as the bath is used and accumulates metallic impurities. Sulfate is often determined centrifugally, but this method is not always reliable. Excess sulfate in the bath is commonly precipitated by the addition of barium carbonate, but it can also be counterbalanced by the addition of chromic acid, if convenient.

A recent important development is the introduction of new chromium plating bath systems called self-regulating high speed, or simply S.R.H.S., baths. These are chromic-acid-type solutions containing mixed and cooperating catalyst acid radicals in automatically controlled concentration by virtue of solubility characteristics of the special addition agents used. The advantages and results to be obtained have been described by Stareck, Passal, and Mahlstedt.⁵¹

Fluosilicate-containing chromium plating baths are more difficult to analyze and control, and this is one reason why they have not been more frequently used. Many methods have been proposed, but none of them seems to have the advantages of simplicity, dependability, speed, and accuracy in sufficient measure. Wallbank indicated⁵² that no methods are available. As mentioned above, Bilfinger³⁰ considers such baths unstable, although he also suggests methods of analysis.* There is considerable confusion and inaccuracy in the literature relat-

* See Reference 30; also Reference 47, 2nd ed.

ing to fluoride- and fluosilicate-containing chromium baths, partly as a result of the persistent use of glass containers by most workers.

ANODES

Insoluble lead anodes are almost always used in chromium plating from chromic acid baths. The film of lead peroxide which forms on these anodes during use causes the trivalent chromium to be reoxidized continuously to chromic acid, thereby maintaining its concentration at a low value.

Anodes of chemical lead can be used, but they are attacked by the solution and cause the formation of excessive amounts of lead chromate sludge. Antimonial lead is preferable to chemical lead because of its greater corrosion resistance and strength.⁵³ Lead-tin alloys have the highest corrosion resistance and are recommended as the best available material for anodes and temperature-control coils.⁵⁴

Lead and lead alloy anodes of varying cross section have been proposed from time to time, but for most work ordinary flat anodes are satisfactory. In general, it is preferable to use a number of narrow anodes rather than a single wide sheet, as in this way more uniform current distribution is obtained. It is important to use thick enough anodes to conduct the high currents required for chromium plating. Anodes that are too thin will overheat in use and tend to corrode and warp excessively.

Many anode materials other than lead alloys have been tried, but nothing better has been found.⁵⁵⁻⁵⁷ It is perhaps worthy of note that pure iron, such as Armco iron or electrolytic iron, is corroded less as anode than steel or nickel. Iron anodes have occasionally been used, particularly in industrial chromium plating, in special instances where greater strength and rigidity than obtainable with lead is desired. However, their continued use leads to the accumulation of iron and trivalent chromium in the bath. Where iron anodes are used, it is recommended that they be coated with lead whenever it is feasible to do so. Small platinum wire anodes can also be used for special purposes, such as plating the inside of very small openings, like those of wire-drawing dies.

Recent workers also recommend lead-silver alloys. Ishida⁵⁸ found improved corrosion resistance by lead anodes containing up to 3 to 5% silver. Gebauer⁵⁹ claims six times longer life for lead anodes containing 2% Ag and 2% Sn, compared to ordinary 6% Sb anodes. Niles⁶⁰ claims best results with 6 to 12% Ag, and states that the sur-

face coating formed on such alloys has a conductivity equal to that of a chromium plating bath.

Lead anodes used in chromium plating cannot have too heavy or irregular a coating of lead peroxide on them, or the current distribution may be affected. It is customary to clean anodes regularly, especially those used in heavy hard chromium plating which conform closely to the article being plated. The cleaning is done by means of acid dips and scratch brushing, but is difficult and time consuming, and frequently not all the semi-insulating coating is removed. Hyner⁶¹ discovered an easy and efficient method consisting of electrolytic reduction of the coating to metallic lead by cathodic treatment in an alkaline pyrophosphate solution.

EQUIPMENT

Tanks for chromium plating have for years been made of lead-lined steel. Antimonial lead linings have been widely used because their corrosion resistance in chromic acid solution is greater than that of chemical lead. Tin-lead linings are superior to antimonial lead in corrosion resistance.⁵¹

Acid-proof brick linings have also proved very satisfactory for chromium plating tanks made of steel. This type of lining has excellent resistance to the corrosive action of the plating bath. The silica cements used in laying the brick are somewhat porous, and for this reason thin joints with a thickness of only about $\frac{1}{16}$ to $\frac{1}{8}$ in. are used. This type of lining has the advantage of being a non-conductor, thereby minimizing stray current effects. The life of such linings is excellent, especially when the steel tank is first coated with suitable lacquer.

The acid-proof brick lining is similar to wire-glass linings, which are sometimes used abroad. These should not be confused with the use of separate glass sheets to cover much of the sides and bottom of steel tanks to prevent stray currents and short circuits.

Another type of lining which appears to be giving satisfactory service consists of flexible synthetic resin sheets (plasticized polyvinyl chloride) cemented to a steel tank and welded together. This type of lining saves space compared to a brick lining but is generally not recommended for temperatures above 60°C.

Special insulating materials of the vinyl type have been developed⁶² to withstand the action of chromium plating solutions, as the latter dissolve nitrocellulose and most organic resins. These insulators are used in solid form in the construction of composite racks and in liquid

form for coating ordinary racks or stopping off portions of the work which it is desired not to plate. The use of insulated racks results in a saving of power and chemicals and gives much better plating. The use of a stop-off is particularly important in industrial chromium plating, where it is frequently desired to plate only certain surfaces of an object to a definite thickness and to leave other surfaces unplated.

Owing to the relatively high current densities used in chromium plating, it is necessary for all components of the circuit to be of sufficient size to carry the amperage required without overheating or excessive voltage drop.

HYGIENE

The large volumes of hydrogen and oxygen evolved during chromium plating cause a chromic acid spray to be given off which, if permitted to escape into the plating room, is damaging to the surroundings and constitutes a health hazard. The chromic acid is sharply irritating, and corrosive to the mucous membranes of the nose and throat. This spray, therefore, requires removal to protect the workmen and equipment, and adequate exhaust facilities must be provided for the purpose.

The requirements in this connection were investigated by Bloomfield and Blum⁶³ and Riley and Goldman⁶⁴ among others. They concluded that the concentration of chromic acid should not be permitted to rise above 1 mg/10 cu m of air. These requirements have been adopted by the American Standards Association.⁶⁵ Comprehensive discussions of exhaust systems for chromium plating tanks have been published.⁶⁶⁻⁶⁷

Many measures have been proposed to replace or supplement the necessary exhaust hoods, and to save some of the chromic acid and heat losses which these entail.^{68, 69} The more recently proposed use of a layer of floating plastic beads^{70, 71} or of wetting agents⁷² may in some cases offer a partial solution to the problem, but it is in general not possible to dispense with an adequate exhaust system.

Studies of industrial dermatitis, including skin conditions arising in workers exposed to chromates or chromic acid, have been published by Schwartz,⁷² Macchia,¹⁶ and Wilkerson⁷³ among others. The remedies suggested include avoidance of contact with the irritating chemicals, cleanliness, thorough washing, use of protective and healing salves and ointments, and visits to a physician when necessary.

The disposal of waste waters containing chromic acid is a problem of increasing importance. It has been reviewed at length by several authors,^{74, 75} and will not be discussed here.

CHROMIUM PLATING SMALL PARTS

Small parts such as screws, nuts, bolts, and rivets can be chromium-plated in wire mesh baskets or by stringing them on wires. Stringing on wires or racking is convenient for articles of moderate size, perhaps

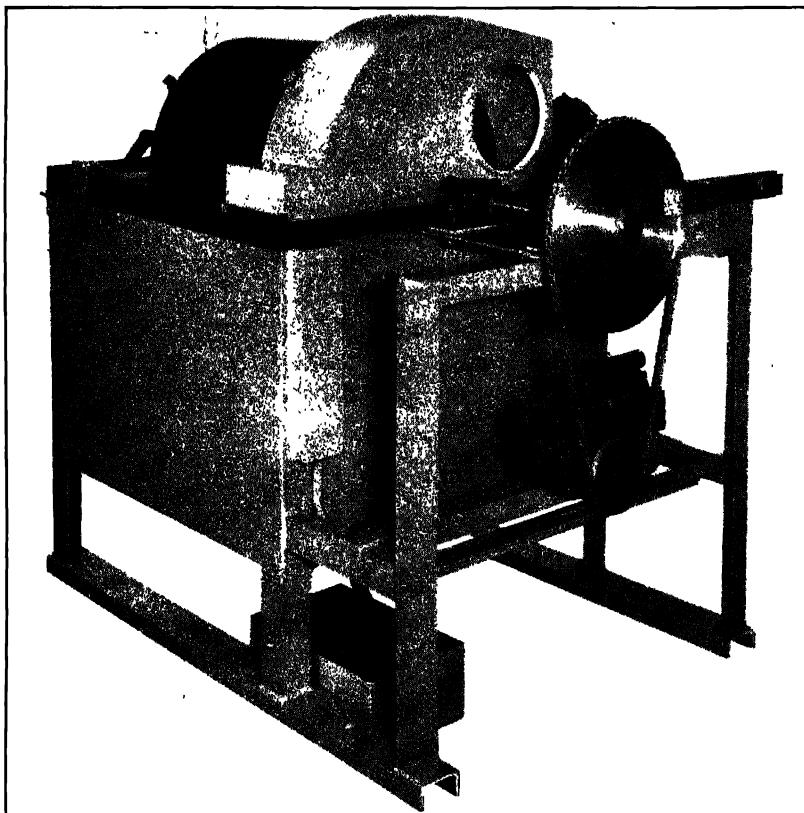


Fig. 4. Large-batch chromium plating barrel.

1 in. in length or longer. For basket plating, horizontal copper wire mesh trays are generally used with a rim about 0.5 in. high soldered to a frame for suspension from the cathode rod. The small parts are spread in a thin layer on the wire mesh tray so that they do not cover each other, and the whole plated at as high a current density as possible without burning—for 5 to 10 min. Generally the entire basket is shaken or jarred a little a few times during plating, to cause the small parts to shift position and avoid contact marks. Flat parts which fit

closely on top of one another do not lend themselves readily to basket plating. A paper on basket chromium plating was published by Ingersoll.⁷⁶

Many attempts have been made to develop a barrel for chromium plating, but most of them have ended in failure. This probably is due for the most part to the unusual electrochemical and mechanical difficulties involved. Chromium plating barrels of both the batch and continuous types have been described⁷⁷ and are operating successfully in several plants. Figure 4 shows a large batch type of barrel of recent design. A rotating horizontal cylinder is used with a specially designed inside anode. The barrel plating time, for decorative purposes, is about 10 minutes, but heavy hard chromium plates can also be produced in the barrel by using longer plating times.

PREPARATION OF BASIS METALS

The cleaning of work to be chromium-plated for bright or decorative finish (as distinguished from work for thick deposits or for industrial applications) may be divided into two general classifications, wet cleaning and dry cleaning. Typical wet cleaning consists in putting the work successively through an alkaline cleaner solution, a water rinse, an acid dip, and a water rinse. Dry cleaning consists in wiping the work on a buff wheel or by hand, without dipping it in solutions of any kind.

Where wet cleaning is feasible, it often gives better results than dry cleaning. Wet cleaning is preferred and recommended for its effectiveness in preventing gray streaking and spotting of the chromium plate. The principal features of wet cleaning procedures are cathodic alkaline cleaning and acid dipping. Both of these steps help to remove any oxide or tarnish on a nickel surface, whether visible or invisible, and result in "activating" the nickel or making it easier to chromium plate. Nickel surfaces are considered "passive" if they are oxidized and difficult to cover with a bright chromium plate. Cathodic alkaline cleaning is quite effective in removing this condition if it is not too severe. Acid dipping is even more effective. Typical acid dipping procedures are:

1. Immersion in 30 to 50% by volume HCl for 30 to 60 sec.
2. Immersion in 20% by volume H₂SO₄ for about 5 min.
3. Treatment as cathode at 4 to 6 v in 5% by volume H₂SO₄ for about 15 sec.

Where wet cleaning is not feasible, the plater must sometimes resort to dry cleaning. The success of the dry cleaning procedure depends

on the fact that the chromium plating solution itself serves to some extent as both cleaner and acid dip. The vigorous evolution of gas during plating, together with the strong cleansing action of the hot chromic acid, tend to break down light dirt films. If the dirt, grease, and oxide are excessive, the cleansing action of the plating solution is overtaxed, with the result that the chromium plate is defective.

Bright nickel plate which has not been buffed may have an oxidized surface or the equivalent, even in the as-plated condition. Even though no visible film of oxide is apparent, the surface may be "passive" or difficult to cover with bright chromium plate. When this occurs, the above wet cleaning procedures are desirable or necessary for good results.

The importance of a satisfactory wet cleaning procedure for nickel surfaces has been confirmed by Tucker and Flint,⁷⁸ who also review some of the previous work in this field. Cathodic electrolytic cleaning is also helpful, and special solutions and procedures are sometimes used.⁷⁹ Anodic cleaning in the usual alkaline cleaners must be scrupulously avoided, as it will oxidize nickel surfaces and make them impossible to chromium plate.

Heavy chromium deposits used in industrial or hard chromium plating usually require extraordinarily good adherence to the basis metal because the plated articles are often subject to severe strains in service. A high degree of adherence of chromium to steel can be obtained by electrolytic cleaning or etching of the steel surface prior to chromium plating. A satisfactory etch is obtained by treatment of steel parts as anode at 6 v in chromic acid solution or in the plating bath. Anodic etching in about 50°Bé sulfuric acid at room temperature for about 1 min is also used. Additional details for the preparation of steel for heavy chromium plating are given in a Recommended Practice of the American Society for Testing Materials.⁸⁰

Zmihorski⁸¹ has investigated the adhesion of heavy chromium deposits on steel; he finds that an adhesion of about 25 to 28 tons/sq in. is obtained by the usual hard chromium plating procedures. He also finds that etching in sulfuric acid gives somewhat better adhesion than etching in chromic acid; that a low current density gives somewhat better adhesion than high current densities; that thin deposits are better than thick; that deposits from pure solutions containing no iron and trivalent chromium are better than those from contaminated solutions; that fluosilicate are better than sulfate-type solutions; and that heat treatment appears to have no effect on adhesion.

High carbon cast irons and steels may be difficult to chromium plate directly if subjected to acid pickling prior to plating. Pickling

apparently develops a low overvoltage surface condition which makes it easy to deposit hydrogen and difficult to plate chromium. It is therefore recommended that acid pickling be avoided in such cases, and that sandblasting or other methods of cleaning be used.

Zinc and zinc-base die castings are commonly chromium plated for decorative purposes after previous nickel, or copper and nickel, plating. If the castings are satisfactorily nickel plated, the chromium plating is the same as for nickel-plated copper, brass, iron, steel, or other basis metals. If the nickel plate directly applied on a zinc-base article does not completely cover it or is too thin, it will be difficult or impossible to deposit chromium at or near these bare or too thinly plated points. A remedy for such a difficulty is to plate a substantial thickness of copper under the nickel. There is a certain amount of chromium plating directly on zinc die castings, but generally such plating is for wear purposes.

TESTS OF DEPOSITS

For decorative chromium plating, a thickness of about 0.00001 to 0.00002 in. (0.00025 to 0.00050 mm) is generally used. This corresponds to about 2 to 4 min plating time under the bright plating conditions generally used. It might seem desirable to apply a heavier chromium plate, but, unless quite thick deposits are used, the plates are more porous and less corrosion-resistant than the thin plate mentioned above. This is probably due to the fact that thin deposits build up normally at first and have only simple pores, but, after a thickness of about 0.00002 in. has been deposited under the usual conditions, the shrinkage strains in the deposit²⁷ become sufficient to start cracking it open in fine hair-line cracks extending down to the basis metal. Then the deposit is less resistant to corrosion than the thinner deposit of 0.00002 in. or less, which has no cracks. As the thickness of chromium plate is increased still further (0.0005 in. and over), the metal deposits over the cracks first formed, and, whereas additional cracks continue to occur, most of them do not extend to the basis metal. Heating accentuates the cracking. The cracks are not associated with any lack of adherence of the deposit, and they do not cause any peeling unless corrosion sets in underneath the chromium plate and releases it in flakes.

These phenomena were pointed out by Baker and Pinner,²² who used a copper plating test developed at an early date by Dubpernell in order to study the type of porosity involved. An important precau-

tion in connection with this test is to apply it only to articles completely covered with chromium, or to insulate all areas not chromium plated. Otherwise, all the copper will deposit on the areas not covered by chromium, and none will plate on the pores or cracks in the chromium plate. Another way of meeting this difficulty is to increase the voltage during the acid copper plating step until some

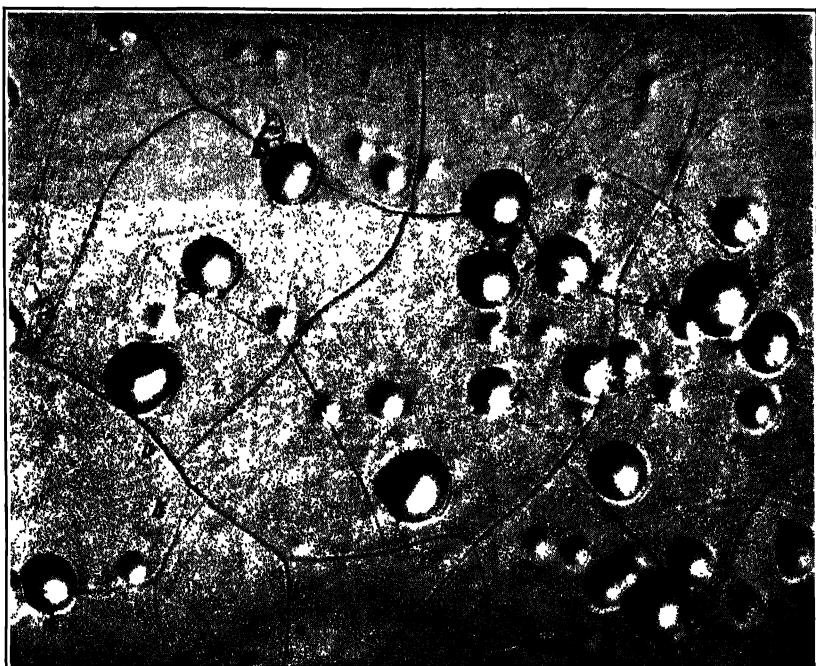


Fig. 5. Thick bright chromium plate, 1000 \times .

copper is deposited on the chromium-plated areas on pores or cracks, or both.

Additional studies of the porosity and cracking of chromium plate were reported by Grant and Grant,⁸³ Baker and Rente,⁸⁴ Barrows,⁸⁵ Blunn, Barrows, and Brenner,⁸⁶ Mahlstedt,⁸⁷ Jacquet,⁸⁸ Arkharov and Fedorov,⁸⁹ and Kochergin⁹⁰ among others. The cracks in thicker deposits were made evident by Gebauer⁹¹ by anodic etching in 10% caustic soda solution followed by microscopic examination. Reverse current treatment in chromic acid solution has been employed by Dubpernell as a test for cracks in heavy chromium deposits. Almost any brief treatment is sufficient, a typical treatment being 4 amp/sq in. for 15 sec. Wyllie used the copper plating test to show the cracks

in chromium deposits after tensile testing.⁹² Cohen⁹³ studied the chromium compounds found in the crack network of heavy chromium deposits, particularly after heat treatment and solution of the metal.

Figures 5, 6, and 7 show the surfaces of typical chromium deposits at a magnification of 1000 \times , taken from a research report by T. H. Webersinn and J. M. Hosdowich of United Chromium, Incorporated

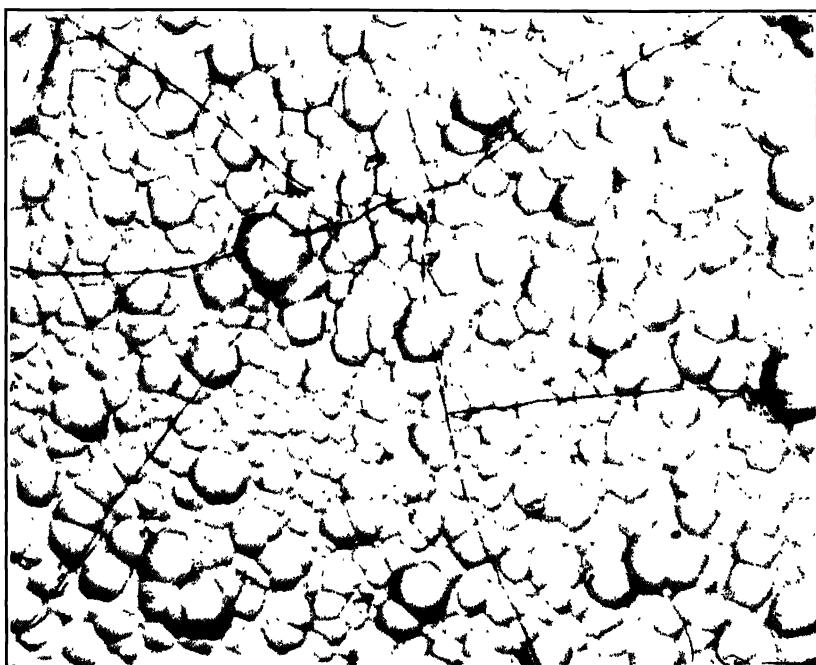


Fig. 6 Semi-bright hard chromium plate. 1000 \times .

(September, 1931). Figure 5 shows the surface of a thick bright plate, with typical cracks in various stages of formation and filling in with further chromium plate. The start of a few nodules is also shown. Figure 6 shows a smooth satin finish or "bubbly" type of plate formed at a higher current density, typical of deposits frequently used for hard chromium plating. Figure 7 shows a crack-free, slightly "milky" type of plate such as is produced by means of the Mahlstedt process.⁸⁷

A very thin coating of chromium is commonly specified for decorative purposes, and this thin coating is generally applied over nickel plate. Thus the American Electroplaters' Society-American Society for Testing Materials specifications⁹⁴ state that the minimum thickness

ness of the chromium coating shall be 0.00001 in. (0.00025 mm) and that the average thickness required in order to yield a minimum thickness of 0.00001 in. will almost always be at least 0.00002 in. A recent Federal specification⁹⁵ for plumbing fixtures calls for an average thickness on each fitting of at least 0.000018 in. of chromium, or



Fig. 7. Crack-free "milky" low current density chromium plate. 1000X.

a minimum thickness on significant surfaces of at least 0.00001 in. Either requirement may be met. A U. S. Army specification requires only a minimum thickness of 0.00001 in.⁹⁶

A British Standard⁹⁷ has also been issued which covers decorative nickel and chromium coatings, and, according to Hothersall,⁹⁸ calls for an average thickness of chromium of not less than 0.00002 in. This is somewhat heavy if cracking is to be avoided.

Accelerated corrosion tests as a rule are not carried out on chromium plate per se. Since chromium plate is not ordinarily used alone for decorative purposes, but is used in composite plates with nickel or copper and nickel, tests on such coatings result in data on the com-

bined corrosion resistance of the composite deposit. When properly applied, chromium plate adds substantially to the corrosion resistance of the combined coatings.

Dissatisfaction with only the results of accelerated tests led to an extensive series of outdoor exposure tests begun in 1932 and sponsored jointly by the American Electroplaters' Society, the American Society for Testing Materials, and the National Bureau of Standards. Numerous reports on the results of these tests appear in the publications of the societies concerned, and in those of the Bureau of Standards.⁹⁹ The Bureau also studied accelerated and porosity tests for comparison with outdoor exposure tests.¹⁰⁰

In general, the salt spray test is still the most widely used accelerated corrosion test. It is briefly described as part of the A.E.S.-A.S.T.M. specifications.⁹⁴ There has been considerable effort in recent years to revise and standardize this salt spray test. It was described in considerable detail in a publication of the Bureau of Standards,¹⁰¹ a combined Army-Navy specification was issued,¹⁰² and a separate tentative standard was published by the American Society for Testing Materials.¹⁰³ A specification was also issued by the Quartermaster Corps.¹⁰⁴ Other investigations of the factors affecting the results in the salt spray test have also been made.¹⁰⁵⁻¹¹⁰

The ferroxyl test is also used to determine the porosity of chromium plate.^{86, 100, 111, 112} However, as reported by Pinner and Sperry¹¹³ and Strausser¹¹⁴ and others, the test requires considerable care in use and in the interpretation of results.

Generally, the average thickness of chromium coatings is determined by dissolving off the coating from a known area and determining the amount of chromium based on chemical analysis. The thickness of decorative chromium plate is usually too small for ready determination by microscopic or magnetic methods. Blum and Olson¹¹⁵ improved the spot test, using the rate and time of solution in hydrochloric acid to determine the local thickness of thin chromium coatings. The test is described in detail in the A.E.S.-A.S.T.M. specifications,¹¹⁶ in a Federal specification,* and in a British Standard.⁹⁷ Spencer-Timins¹¹⁷ investigated the best endpoint for this test. The electrographic method can be applied to the determination of the thickness of thin coatings of chromium and other metals.¹¹⁸ The change in potential occurring when the coating has been stripped

* Reference 95, pp. 113-114.

anodically from a limited area shows the time of stripping with a fixed current and 100 per cent anode efficiency.

HARD CHROMIUM PLATING

The literature on this subject has become so extensive that nothing resembling a complete review can be attempted here. During World

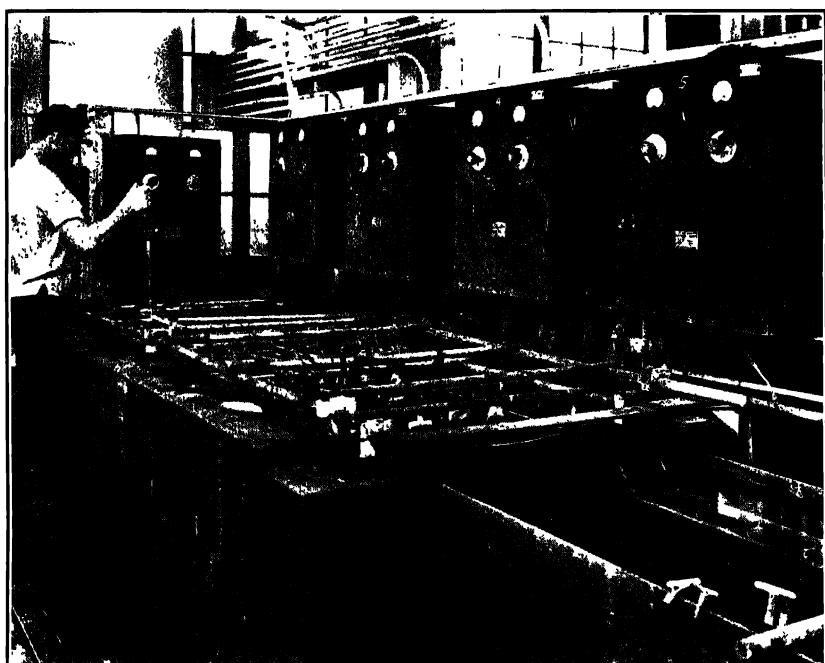


Fig. 8. Tank for hard chromium plating small tools, divided into five bays, with separate rectifiers for each.

War II Kolodney¹¹⁹ wrote an excellent review with over 300 references, but much has appeared since that time. Unfortunately, Kolodney's review is not readily available, even though it was abridged and released for publication.¹²⁰ Bilfinger's⁴⁷ excellent book has appeared in a second edition. Gillet¹²¹ published a good general review of the subject before the war.

The French established a "Centre d'Information du Chrome Dur" after the war, and P. Morisset of this center published a useful review of applications, together with a bibliography and abstracts of more than 1000 references.¹²² He has also published a general book on

hard chromium plating.¹²³ Several annual collections of papers have also been published by this agency,¹²⁴ in addition to a monthly bulletin. Good general articles were published by Hosdowich¹²⁵ and Coyle.¹²⁶ Figure 8 shows a typical hard chromium plating plant.

The success of chromium plate in industrial applications is probably to be attributed to its unique combination of properties not possessed by any other one material available commercially. The most important of these properties are the hardness, corrosion resistance, low coefficient of friction, non-galling and non-wetting qualities. In many instances all these properties are important for successful commercial application.

The hardness alone would not be sufficient to secure widespread use, as there are available a number of other hard materials or hardening processes. It is the combination of very great hardness with extremely good corrosion resistance (equal or superior under most conditions to that of such noble metals as gold or platinum), and very low coefficient of friction or unique surface qualities, which has given such remarkable results in many applications of chromium plate. To this should also be added relative ease of application and control, which insures the maintenance of fixed standards of quality and durability, together with moderate cost.

The benefit of the hardness of chromium deposits is not effectively obtained unless the coating is deposited on a sufficiently hard basis metal and to a satisfactory thickness. Generally, hardened steel is used for the basis metal. Even a relatively heavy deposit of chromium may be crushed or indented if applied over a soft basis metal such as copper. The best possible adherence is also important in many uses where the surface may be subjected to severe strain or shock, and any chipping of the deposit would be injurious. Table 4 gives basis metal hardnesses and thicknesses of chromium plate suggested for different applications.

The low coefficient of friction and desirable surface properties of chromium are realized for the most part only on relatively smooth surfaces. Frequently, chromium deposits are ground or lapped to size. The technique of grinding chromium plated parts has been reviewed by several authors.¹²⁸⁻¹³⁰ Sometimes a bright deposit is applied to a smooth surface and used without further mechanical treatment. By means of careful operation it is possible to plate to size within very close limits. Worn machine parts are salvaged by chromium plating them to size.

Some of the outstanding applications of industrial chromium plate include gages, tools, and machine parts generally, both new parts and

TABLE 4¹²⁷

Application	Recommended Rockwell C Hardness	Thickness, in.
Drills	62-64	0.00005-0.0005
Ramers	62-64	0.0001-0.0005
Burnishing bars	60-62	0.0005-0.003
Drawing plugs or mandrels	60-62	0.0015-0.008
Drawing dies	62 inside 45 outside	0.0005-0.008
Plastic molds	55-60	0.0002-0.002
Gages	48-58	0.0001-0.0015
Pump shafts	55-62	0.0005-0.003
Rolls and drums		0.00025-0.012
Hydraulic rams		0.0005-0.004
Printing plates (engraved steel)		0.0002-0.0005

the plating or replating of worn parts for salvage purposes. Taps, reamers, drills, saws, milling cutters, burnishing tools, etc., have all been successfully plated. Molds for plastics and rubber are plated to reduce wear and sticking, and to improve the appearance of the product. Drawing dies and mandrels, coinage dies, rolls for cold-rolling metals to a high luster, calendar rolls for various materials and printing and engraving dies are other examples of common uses. Gun barrels are frequently plated for the maintenance of accuracy over a long period of use, as with anti-aircraft guns.^{131, 133, 35} Pump shafts and the cylinders of internal combustion engines have been plated with good results. The list of special uses could be extended almost indefinitely.

In each application the most desirable thickness of chromium and hardness of the basis metal have to be determined empirically by trial and error, with the aid of previous experience. If high corrosion resistance is desired in addition to wear resistance, as with rotary driers for corrosive chemicals and with paper mill machinery, relatively thick deposits of at least several thousandths of an inch are required (0.001 in. = 25.4 μ). Sometimes substantial undercoats of nickel or copper are used in such applications also.

Hard chromium plate has been found useful on basis metals of widely varying hardness, although the basis metal should generally be as hard as possible. Thus, on one end of the scale, good results have been obtained by chromium plating cutting tools tipped with tungsten carbide.¹³⁴ On the other hand, zinc alloy dies for auto stampings have been chromium plated for longer life,^{135, 136} and the hard chromium plating of aluminum has received considerable development, especially in connection with small internal combustion engine

cylinders.^{137, 138} A series of outstanding publications on the hard chromium plating of aluminum have appeared, mostly in German.^{139-143, 47} The detrimental effect of hard chromium plate on the fatigue strength of the aluminum has also been investigated extensively.¹⁴⁴⁻¹⁴⁶

Hard chromium plate reduces the fatigue strength of steel markedly. Investigations of this effect have been reviewed by Kolodney.^{119, 120} Additional extensive investigations were made by Cüppers,¹⁴⁷ Mehr et al.,¹⁴⁸ Bastien and Popoff,¹⁴⁹ Wellinger and Keil,¹⁵⁰ Eilender et al.,¹⁵¹ and Logan¹⁵² among others. Dubpernell¹⁵³ developed a special type of crack-free chromium deposit to minimize the loss of fatigue strength of steel plated therewith. Sinnott¹⁵⁴ has reported less loss of fatigue strength of steel plated with chromium from the new S.R.H.S. baths.

The use of a softer deposit produced at higher solution temperatures and with some modifications of solution composition has been proposed,^{155, 159, 35} but it does not seem to have been used commercially to any noteworthy extent, perhaps because of the high current density required.

Several specifications have been issued covering hard chromium plating,¹⁶⁰⁻¹⁶² but it is difficult to standardize the operations in this rapidly growing field. The original Army-Navy Specification in 1942 called for a minimum Vickers hardness of 700 under a 1-kg load, but this requirement has been eliminated. The S.A.E. Specification¹⁶¹ calls for a chromium plate having a hardness of not lower than 700 Vickers or the equivalent.

POROUS CHROMIUM PLATE

This name has been given to modified chromium deposits with oil-retaining properties, used on internal combustion engine cylinders and piston rings. Such deposits were used especially during the war on aircraft and diesel engines for salvage, and to make the engines last longer. Three main types of "porous" chromium plate have come into common use.

The first is the "mechanical" type produced by grit blasting the basis metal, chromium plating, and final finishing to size by grinding, honing, or polishing.¹⁶³ The second and third types are the "pitted" and "channel" porosity. Both are obtained by treating the chromium deposit in an etching solution. The type of porosity obtained is dependent upon careful control and regulation of the conditions of chromium deposition. Numerous publications and patents describe

the production of all these types of porous chromium plate and the results obtained with them.¹⁶⁴⁻¹⁸⁷

The "pit" type of porous chromium may be produced, for example, by plating under ordinary hard chromium plating conditions such as in a bath containing 33 oz/gal chromic acid and 0.3 oz/gal sulfate, at 50°C, and treating the resultant deposit as anode or cathode in a suitable etching solution, or by simple immersion in acid. After the deposit has been heavily attacked, numerous cracks are found to be eaten away, and a surface crust of undermined metal remains. When this crust is ground, honed, or polished away, numerous pits remain in the chromium plate.

Good conditions for producing the "channel" type of porous chromium plate are 60°C and a ratio of chromic acid to sulfate of 115:1. The usual current densities of 3 to 4 amp/sq in. are employed. After treatment in the etching solution, the deposit does not have a loose surface crust but only a network of fissures, so that grinding, polishing, or honing leaves channels, with dense chromium "plateaus" or "lands" between. This type of porous chromium has been largely used for aircraft engine cylinders, while the pit type has been more extensively employed in diesel engines and on piston rings. Several specifications have been issued on porous chromium plating.¹⁸⁸

OTHER SPECIAL TYPES OF CHROMIUM PLATE

In the early days of commercial development the smooth mouse-gray chromium plate obtained from cold solutions was sometimes used, principally because of ignorance of the best conditions for bright plating. This deposit could be buffed bright, but at much more cost than plating under bright plating conditions.

A "frosty" or satin-finish plate in between the above two types was found desirable by Mason¹⁸⁹ for press plates. Trist used a special cold chromium plate produced in refrigerated electrolytes for printing plates.¹⁹⁰

Many attempts have been made to produce "black" chromium plate, and such deposits have been used industrially. They are dark gray rather than black, however, and all dull or matte chromium deposits seem to turn bright metallic rather readily if exposed to much abrasion or wear, in spite of the hardness of the metal. An outstanding "black" chromium plate was that of Siemens and Halske, A.G., produced by using a high current density in a cold bath containing principally chromic acid and acetic acid.¹⁹¹⁻¹⁹⁴

Carveth obtained a black color on chromium deposits by immersion in molten cyanide.¹⁹⁶ The carburizing of chromium deposits for greater hardness has also been frequently attempted.^{196, 197} Although this is something of an anomaly and the plate is first softened by the heat, it does appear possible to obtain very hard chromium carbide coatings.

Many attempts have been made to work out processes for chromium plating from bivalent and trivalent solutions, but no commercially satisfactory solution has been published. There have also been numerous attempts to plate chromium alloys, and fused baths have been described, but nothing useful appears to have come from such work. The U. S. Bureau of Mines has recently developed a process for the electrowinning of pure chromium metal from the ore, using a mixed bivalent and trivalent chromium sulfate solution,^{198, 199} but the process

TABLE 5. SPECIFIC GRAVITY AND DEGREES BAUMÉ OF CHROMIC ACID SOLUTIONS AS A FUNCTION OF THE CrO₃ CONTENT *

Sp. Gr.	De- grees Baumé	CrO ₃ Content			Sp. Gr.	De- grees Baumé	CrO ₃ Content		
		Molar- ity	oz/gal	g/l			15° 4° C	Molar- ity	oz/gal
1.01	1.44	0.15	2.0	15	1.18	22.1	2.57	34.4	257
1.02	2.84	0.29	3.9	29	1.19	23.2	2.72	36.4	272
1.03	4.22	0.4	5.8	43	1.20	24.2	2.88	38.6	288
1.04	5.58	0.57	7.6	57	1.21	25.2	3.01	40.3	301
1.05	6.90	0.71	9.5	71	1.22	26.2	3.16	42.3	316
1.06	8.21	0.85	11.4	85	1.23	27.1	3.30	44.3	330
1.07	9.5	1.00	13.4	100	1.24	28.1	3.45	46.2	345
1.08	10.7	1.14	15.3	114	1.25	29.0	3.60	48.2	360
1.09	12.0	1.29	17.3	129	1.26	29.9	3.75	50.2	375
1.10	13.0	1.43	19.1	143	1.27	30.8	3.90	52.2	390
1.11	14.4	1.57	21.0	157	1.28	31.7	4.06	54.5	406
1.12	15.5	1.71	22.9	171	1.29	32.6	4.22	56.5	422
1.13	16.7	1.85	24.8	185	1.30	33.5	4.38	58.7	438
1.14	17.8	2.00	26.8	200	1.30	34.3	4.53	60.7	453
1.15	18.9	2.15	28.8	215	1.32	35.2	4.68	62.7	468
1.16	20.0	2.29	30.6	229	1.33	36.0	4.84	64.8	484
1.17	21.1	2.43	32.6	243	1.34	36.8	5.00	67.0	500

* From data compiled by J. A. Beattie for *International Critical Tables*, McGraw-Hill Book Co., New York.

has not been adopted for plating purposes. A two-compartment cell is used, and continuous operation on a large scale seems necessary for good results. It is reported that the pilot plant is producing about 70 lb per day of pure chromium metal in cathode flakes about $\frac{1}{16}$ to $\frac{1}{8}$ in. thick, with a smooth but dull surface; this metal is available for metallurgical test purposes.

PROPERTIES OF CHROMIUM PLATE

CLOYD A. SNAVELY * AND CHARLES L. FAUST *

STRUCTURE

Chromium plate is unique among the metal plates extensively used in commerce because of the important bearing the structure of the plate has upon its uses and performance. Actually, many variations in structure and physical properties can be obtained by proper adjustment of the plating conditions and post-plating treatments. The theory underlying these structural characteristics is reasonably complete and will be outlined herein. An understanding of the theory is useful in choosing the proper plate for a given service.

Chromium plate 0.00002 in. (0.5μ) or less in thickness is normally porous, whereas thicker plate is "cracked."^{1,2} The surface of thick plates is usually smooth and bright appearing to the unaided eye. However, when viewed under the microscope at magnifications of the order of 100 \times or greater, the surface is revealed as having numerous dome-like projections. Figure 1 shows a typical surface. Figure 2

* Battelle Memorial Institute, Columbus, Ohio.

shows the same surface at higher magnification. The crack pattern is clearly shown along with vestiges of "plated-over" cracks. All conventional plates more than 0.00002 in. thick are cracked in this fashion. Magnifications of 400 \times or greater are usually necessary to show up the cracks.

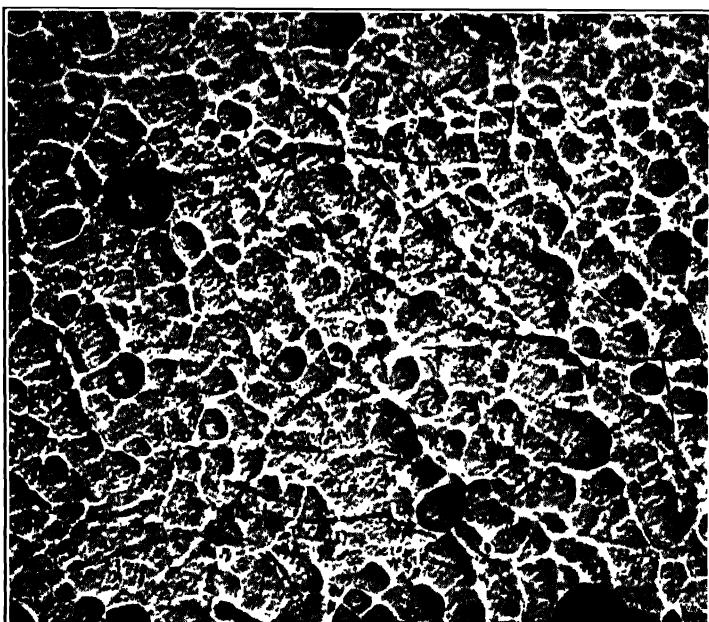


Fig. 1. Surface of "hard" chromium plate showing crack system and nodular appearance. Bath composition: 33 oz/gal CrO₃; 0.33 oz/gal SO₄²⁻. Bath temperature 60°C. Current density 1.8 amp/sq in. Plating time 7 hr. Nodular appearance is emphasized by limited depth of focus of microscope at this magnification (200 \times).

Cohen³ clearly illustrated that these cracks are filled with a transparent film which becomes Cr₂O₃ on heating. The film presumably exists in the plate as a hydrated chromic oxide. These inclusion films are predominantly normal to the basis metal surface. Figure 3 shows a typical chromium plate cross section, and Figure 4 shows Cohen's model of the form of the inclusions in the plate. During plating, fresh cracks continually open at the plate surface and then are filled with included material and covered over by newly deposited metal.

The basic cause of the cracks and inclusions was shown by Snavely⁴ to be related to the formation of unstable *chromium hydrides* during the plating operation. Hydrides can be electrodeposited either in the

hexagonal crystal form (formula Cr_2H to CrH) or in the face-centered cubic crystal form (formula CrH to CrH_2). The *hexagonal hydride* is most likely the one formed under normal plating conditions. It decomposes spontaneously to body-centered cubic chromium and free hydrogen. Some of the hydrogen escapes during the decomposition



Fig. 2 Same unetched surface of chromium plate as in Fig. 1. Note the various steps in the formation and covering over of cracks as they are illustrated in this photograph. Freshly formed cracks are very prominently evident. Old cracks are more obscure. Very faint indications of many cracks which are nearly obliterated by covering metal deposit are yet visible on close inspection. Magnification 350 \times .

process. The remainder is occluded in the plate. Data on the structure of the chromium hydrides were given by Snavely and Vaughan.⁵ The normal *structure* of chromium metal is the body-centered cubic crystalline arrangement.

The decomposition of either hexagonal or face-centered cubic chromium hydrides to body-centered cubic chromium involves a volume shrinkage of over 15%. Because the plate is restrained in the plane of the basis metal, surface cracks form normal to that surface. The chemical constituents making up the cathode film are drawn into these

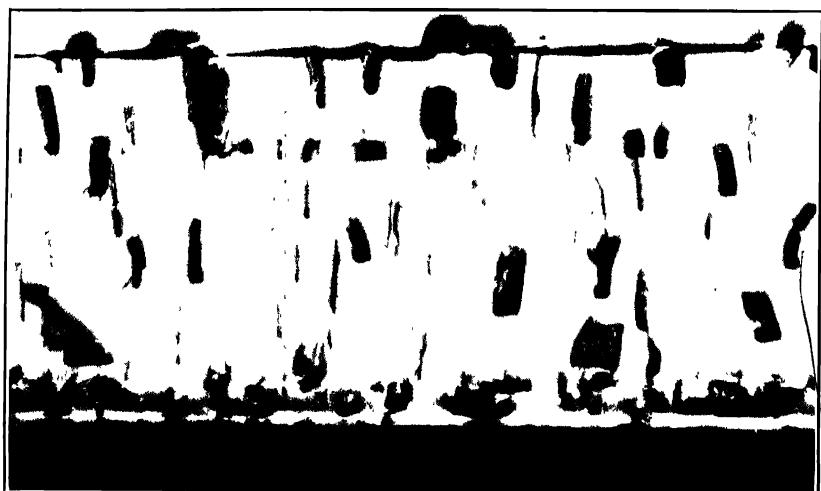


Fig. 3 Cross section of chromium plate shown in Fig. 2. A five-sec electrolytic etch has been applied at 6 v in 10% chromic acid solution at atmospheric temperature. Note form of inclusions. Chromium has been etched away, often allowing inclusions to fall sideways on etched surface of plate. Some inclusions have broken off during the etching process, leaving the cracks they formerly filled visible as thin lines. Inclusions at an acute angle with the etched surface appear as large dark areas. (Magnification 200 \times .)



Fig. 4. Model of the film network in chromium plate constructed with strips of plastic. (From Reference 3.)

cracks and then are bridged over by newly deposited plate. These crack-filling constituents are the inclusion films studied by Cohen.

In addition to the oxide inclusions which are readily detectable by metallographic examination of as-deposited chromium, experimental evidence indicates that there may be additional quantities of oxide finely dispersed through the plate. This dispersed oxide appears to be agglomerated on heating and then may be detected through the microscope.⁶⁻⁸

Wood⁹ measured the grain size of chromium plate by x-ray diffraction methods and arrived at a figure of 14×10^{-7} cm. As a comparison, the smallest grains producible by cold-working metals are of the order of 10^{-4} cm in average diameter. The extremely fine grains in chromium plate have been explained as resulting from the hydride decomposition.⁴

Structural changes taking place on heating chromium plate are those normal for a highly stressed, fine-grained metal as shown by Dale⁶ and Snavely and Faust.¹⁰ Recrystallization takes place on prolonged heating in the temperature range between 300° and 500°C or on shorter exposure at higher temperatures. The new grains are elongated normal to the basis metal. On prolonged exposure at temperatures of the order of 1100°C, large equi-axed grains are formed. During this heating, the inclusion films remain in their original positions, though they are agglomerated into lines of spheroidal particles.

Chromium plate is strongly grain oriented with the (111) plane parallel to the basis metal.¹¹ This preferred orientation persists even after recrystallization.¹⁰ The initial layer of plate is randomly oriented, and the preferred orientation is achieved as plating continues. Chromium plates on polished brass or electropolished steel attain the preferred orientation rapidly, while plates on a machine-ground basis metal receive a relatively thick layer of randomly oriented plate before the preferred orientation appears.

Chromium plating directly on steel normally has a deleterious effect on the mechanical properties of the steel.¹²

With the principles outlined, some of the applications of chromium plate can be examined more closely. The "porous chromium" of commerce is produced by the selective etching of the cracks exposed on the plate surface to give an oil-retentive surface. Thus the poor "wetting" characteristics of chromium plate are counteracted, while the good properties of the plate are unimpaired. "Lo-contraction" chromium plate is deposited at such elevated temperatures¹³ that the hydrides are very short-lived, if they are formed at all. This plate therefore has relatively few cracks and is softer and much less stressed than

conventional chromium plate. Because of these special characteristics, it has exceptional resistance to hot corrosive gases. For the same reasons, it is too soft for applications requiring maximum mechanical erosion or abrasion resistance.

As in plating other metals for engineering uses, chromium plate should be tailored to suit the application. The difference in performance between good and bad selection of plating conditions may often dictate whether or not the plate can fulfill the requirements of a particular application.

PHYSICAL PROPERTIES OF CHROMIUM PLATE

HARDNESS

Fully annealed chromium metal is very soft, and the inherent hardness of chromium plate is an important property relating specifically to the plating process. There is much controversial information in the literature on the hardness of chromium plate. Most of the data reported were probably approximately correct for the specific deposits studied. However, few investigators gave attention to the fact that the hardness of the plate varies according to the plating conditions. Also, a reliable hardness measurement on any deposit can be made only if the indentor avoids the cracks. Therefore the only suitable indentation techniques are those involving use of a microscope to position the indentor to avoid cracks. The Vickers, Eberbach, Knoop, and other commercially available devices provide this feature. The various scratch-testing devices are reasonably reliable, since the actual measurements may be made clear of the influence of cracks.

Using the best-known techniques, several investigators have shown that the hardness of bright chromium plate is about 1000 Brinell or Knoop numbers. Hosdowich¹⁴ studied plates with hardnesses ranging from 600 to over 1000 Brinell. The softer deposits were dull. Hubbard,¹⁵ using a 100-g load on the Knoop indentor, reported a hardness range from 700 to 1200 Knoop numbers, depending on the plating conditions. Brenner, Burkhead, and Jennings⁷ made Knoop hardness measurements, using loads up to 500 g, on deposits from widely varying plating conditions. Values from 300 to 1000 Knoop numbers were obtained. Snavely and Faust¹⁰ reported Knoop hardness measurements taken on cross-section surfaces of as-plated and variously heat-treated specimens. These measurements varied by as much as 200 Knoop numbers from similarly made measurements on the

surface of the plates. Also, there was some variation in hardness across the cross section of the plates. It was found that the load used on the indentor and the reading microscope magnification had an influence on the Knoop values obtained. Therefore these conditions of measurement should be given along with plating and after-treatment conditions when hardness measurements are discussed.

Hosdowich¹⁴ reported abrasion resistance tests which showed that abrasion resistance parallels hardness for mat or bright plates.

COEFFICIENT OF FRICTION

The low coefficient of friction of chromium plate against other metals is an important factor in its use on shafting, piston rings, internal combustion engine cylinders, and similar applications. The following data, published by the Worthington Pump and Machinery Corp. and F. E. Allen¹⁶ and Arkarov, Tagrubskii, and Nenmonov,¹⁷ illustrate the superiority of chromium in terms of this property.

TABLE 1. COEFFICIENT OF FRICTION FOR VARIOUS METAL COMBINATIONS

Metal	Static Coefficient	Sliding Coefficient
Reference 16		
Chromium-plated steel on chromium-plated steel	0.14	0.12
Chromium-plated steel on babbitt	0.15	0.13
Chromium-plated steel on steel	0.17	0.16
Steel on babbitt	0.25	0.20
Babbitt on babbitt	0.54	0.19
Steel on babbitt	0.30	0.20
Reference 17		
Bright chromium plate on cast iron		0.06
Bright chromium plate on bronze		0.05
Bright chromium plate on babbitt		0.08
Hardened steel on cast iron		0.22
Hardened steel on bronze		0.11
Hardened steel on babbitt		0.19

Kontorovich and Arkharov¹⁸ found that bright chromium plate against cast iron gave a lower coefficient of friction value than mat or burned plates. Graham, Williams, and Wilson¹⁹ showed that the coefficient of friction of chromium plate against steel or cast iron increases rapidly with temperature. They concluded that the increase may be avoided by heat treating before polishing. Their studies related to service on internal combustion engine cylinder liners.

COEFFICIENT OF EXPANSION

Hidnert²⁰ found an average coefficient of expansion of $6.8 \times 10^{-6}/^{\circ}\text{C}$ for electrolytic chromium in the temperature range between 20° and 100°C . The coefficient of expansion at any temperature (t) between -75° and 650°C was shown to be expressed by the formula $a_t = (5.88 + 0.01584t - 0.00001163t^2)10^{-6}$. Within the temperature range -100° to 700°C , the length of a chromium plate specimen is expressed by the formula $L_t = L_0[1 + (5.88t + 0.00774t^2 + 0.00000388t^3)10^{-6}]$. He also noted a linear shrinkage of approximately 1.1% during heating the deposits to 500°C for the first time. During subsequent heating and cooling cycles, the expansion and contraction were normal. Snavely⁴ ascribed the initial shrinkage to relief of internal stress and closing up of voids between crystallites. These voids are a result of the decomposition of chromium hydride.

Because of this unusual behavior, there is little hope that a basis metal for chromium plate can be found which will match the performance of the chromium plate from chromic acid baths, during heating cycles.

MELTING POINT

The melting point of electrolytic chromium depends to some extent on its purity. Smithells and Williams²¹ reported the melting point as 1920°C and suggested that this value is low. Grube and Knabe²² obtained a value of $1890^{\circ} \pm 10^{\circ}\text{C}$. These authors showed that the amounts of oxide normally encountered in chromium plate can affect the melting point, so that no accurate figure is possible.

DENSITY

The density of chromium plate varies according to the amount of oxide in the plate, the number and size of cracks, and the magnitude of internal stress. Brenner, Burkhead, and Jennings⁷ reported a systematic study of the density of chromium deposited under various conditions. Values from 6.90 to 7.21 g/cc were obtained. The oxide content decreased as the density increased. After annealing at 1200°C , the density of the deposits increased to within the range 7.09 to 7.22 g/cc. The density of pure chromium is 7.20 g/cc, as calculated from its lattice parameter. Therefore the reported values over 7.20 can be considered anomalies relating to the precision of the measurements.

Hidnert²⁰ reported a density of 6.93 g/cc for as-deposited chromium, and this value is considered representative of most commercially deposited chromium.

REFLECTING POWER

Coblentz and Stair²¹ studied the reflectivity of chromium plate over a light range from ultraviolet to infrared. For the visible range of light, 4000 to 7000 Å in wavelength, they obtained reflectivity values between 62 and 72%. For ultraviolet light, the reflectivity ranged from 55 to 70%, and for infrared from 62% at 7000 Å to 88% at 40,000 Å. These high reflectivity values are usually retained over prolonged periods of exposure of chromium plate because of the corrosion and tarnish resistance of the plate. The reflectivity is seriously reduced when the plate is exposed to highly corrosive atmospheres.

ELECTRICAL RESISTIVITY

Electrical resistivity, like density, is a measure of the continuity, purity, and general soundness of a metal. The number, distribution, and size of the inclusion-filled cracks in chromium are related to the plating conditions. Therefore the electrical resistivity varies according to the plating conditions. Brenner, Burkhead, and Jennings⁷ reported electrical resistivity values for a wide range of deposition conditions. They showed that an electrical resistivity of about 50 to 60 microhm-cm at 2°C may be expected for conventional chromium plate. After annealing at 1200°C, the oxide inclusions are spheroidized and the cracks in which they originated are no longer continuous. As a result, the resistivity of annealed electrolytic chromium approaches a common value of 13 microhm-cm at 28°C, regardless of conditions of deposition.

INTERNAL STRESS

According to the theory for chromium hydride formation and decomposition during chromium plating, the cracks in the plate are the result of internal stresses exceeding the cohesive strength of the metal. Cracking relieves these stresses to the point where they are no longer of sufficient magnitude to extend the cracks. All thick plates are cracked, and all contain residual internal stress. Thin plates may contain even higher stress because they are restrained from cracking by the basis metal.

Brenner, Burkhead, and Jennings⁷ reported stress values as high as 80,000 lb/sq in. for very thin chromium deposits which were not

cracked. Conventional plating practices produced thicker cracked plates having internal stress of about 17,000 lb/sq in. Plates from a dilute bath at 85°C cracked little and contained stresses of 64,000 lb/sq in. Hume-Rothery and Wyllie¹¹ also measured stress in chromium plate. Values ranged from 0 to 56,000 lb/sq in., depending on plating conditions.

CHEMICAL PROPERTIES

OXIDATION AND TARNISH RESISTANCE

The pleasing blue-white color and the oxidation and tarnish resistance of chromium plate are the main reasons for its wide application in decorative uses. Hardness is also a factor. Actually, chromium plate normally has a very thin oxide film on its surface. This oxide film is so stable, tenacious, refractory, and self-healing that it protects the metal underneath from further oxidation. The plate remains bright at temperatures up to 260°C. On prolonged heating of chromium plate to temperatures of the order of 315°C in air, the oxide film grows in thickness and darkens. At higher temperatures, a black or green-black oxide layer is formed. At temperatures of the order of 1000°C, an oxide layer forms on the surface and an extremely hard chromium nitride layer forms between the oxide and the chemically unaffected portion of the plate.¹⁰

The thin oxide film on chromium plate forms so quickly when plating is completed that tarnishing of the plate is not likely to be encountered. The chromium oxide is a satisfactory protection against sulfides which cause serious tarnishing of silver, copper, or nickel.

CHEMICAL RESISTANCE

The chemical resistance of chromium plate is not so great as might be supposed from its performance in air atmospheres. Chromium is readily attacked by the mineral acids and by reducing solutions in general. It is strongly resistant to nitric acid, which heals the protective oxide film, and nitric acid may be used to dissolve other metals such as copper away from chromium plate.

The chemical resistance of chromium plate may be used to best advantage only if the underlying metal is completely covered.²⁴ For that reason chromium plates for corrosive service should be about 0.00075 in. thick or greater, to insure that the cracks are not continuous to the basis metal which is to be protected.

In general, chromium plate may be applied in the same types of corrosion-resistant service as the high chromium stainless steels at ordinary temperatures, depending on the physical properties required of the basis metal.

7.

Cobalt

HENRY B. LINFORD*

Cobalt coatings are very similar to nickel coatings. Since cobalt metal costs several times as much as nickel, the interest in cobalt plating has been relatively small and intermittent. According to Foerster¹ cobalt plating replaced nickel plating in Germany during World War I but disappeared again thereafter. Berger² indicates some commercial use of cobalt on printing plates because of its hardness, and on mirrors and reflectors because of its high reflecting power and its resistance to oxidation. On this last point, Blum and Hogaboom³ state that cobalt is less resistant than nickel to corrosion attack, by printing inks for example, and it oxidizes more readily at elevated temperatures.

Isaac Adams,⁴ the father of commercial nickel plating, recommended double salts of cobalt with ammonium or magnesium and laid down the same rules for the preparation and operation of cobalt baths as for nickel baths. A summary of the early literature is provided by Watts.⁵ The first detailed study of cobalt plating is reported by Kalmus, Harper, and Savell.⁶ Its main effect was to stimulate interest in high speed nickel plating; it led Watts to the development of his single nickel salt bath.

Cassel and Montillon⁷ and Brewer and Montillon⁸ investigated the effect of pH in single cobalt salt baths containing fluoride. Chaybany⁹ and Moore¹⁰ reported on imperfections in cobalt deposits. Chaybany¹¹ also discussed bright cobalt plating baths.

PRINCIPLES

The baths commonly considered are the single and the double cobalt salt baths; both baths can be operated at much higher current densities than the corresponding nickel salt baths.

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Baths containing fluorides instead of chlorides have been suggested,^{5,7,8} with claims for better buffering and for whiter deposits than can be obtained with straight cobalt chloride baths. However, the simultaneous use of boric acid and hydrofluoric acid in a double cobalt bath results in a tendency toward pitting, pinholes, and poor adherence, whereas hydrofluoric acid alone without boric acid⁹ is beneficial.

Several other cobalt baths have been reported, including cobalt triethanolamine¹² and cobalt sulfamate¹³ baths, both of which may merit further study; cobalt thiocyanate baths,¹⁴ which appeared discouraging; coordination compounds;¹⁵ and fused anhydrous cobaltous chloride baths.¹⁶ Cobalt flakes have been prepared¹⁷ by adding 0.4 to 0.6 g/l $\text{CS}(\text{NH}_2)_2$ to the sulfate bath, then breaking up the deposit by impact grinding.

FUNCTIONS OF CONSTITUENTS OF BATH

The functions of the various cobalt bath constituents appear similar to those of nickel plating baths. The cobalt salts furnish the necessary cobalt ions. As the cobalt content of the bath is increased, both the minimum and the maximum cathode current densities are raised. Difficulties in obtaining good coatings were encountered with single cobalt salt baths⁹ having a low cobalt content, a condition which may well be associated with inadequate pH control or presence of impurities.

Chaybany⁹ suspects that very small amounts of arsenic (>0.001 mg/l) promote porosity and non-adherence. The beneficial effect of boric acid in buffering cobalt plating solutions has been experimentally demonstrated.^{2,6} Fluorides, when added to the cobalt baths, also assist in the buffering.⁷ Citric acid seems to be of little value⁶ in plating cobalt.

Kalmus and co-workers⁶ sometimes obtained a "bright deposit, almost as if buffed," when plating on cast zinc from a cobalt chloride-ammonium chloride bath, indicating that zinc ions may act as a brightener under proper conditions. Chaybany¹¹ recommends a bright plating bath containing, besides the double cobalt salt, both formaldehyde and cadmium sulfate with ammonium acetate and acetic acid. Another bright cobalt bath of Chaybany is composed of the double salt, a large excess of sulfuric acid, and, finally, hydroquinone and sodium hydrosulfite as brighteners. It is stated that hydroquinone may be replaced by pyrocatechol or by methylparamidophenol, and that sodium thiosulfite, sulfite, and bisulfite act similarly to the hydrosulfite in acid solutions.

TABLE 1. BATH FORMULAS

(a) Double cobalt salt, $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	23 oz/gal (175 g/l)
(b) Cobalt sulfate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	67 oz/gal (504 g/l)
Sodium chloride, NaCl	2 oz/gal (17 g/l)
Boric acid, H_3BO_3	about 6 oz/gal (45 g/l)
(c) Cobalt sulfate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	67 oz/gal (504 g/l)
Sodium fluoride, NaF	2 oz/gal (14 g/l)
Boric acid, H_3BO_3	6 oz/gal (45 g/l)
(d) Cobalt chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	7-80 oz (50-600 g)
Ammonium bifluoride, NH_4HF_2	1-16 oz (10-120 g)
Boric acid, H_3BO_3	6 oz/gal (45 g/l)
Water	1 gal (1 liter)
(e) Double cobalt salt, $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	23 oz/gal (175 g/l)
Neutral ammonium acetate	3.5 oz/gal (26 g/l)
Free acetic acid	0.1 oz/gal (1 g/l)
Formaldehyde (38%)	0.35 oz/gal (2.6 g/l)
Cadmium sulfate,* CdSO_4	0.02 oz/gal (0.18 g/l)

* Higher concentration when the temperature exceeds 25°C (77°F).

OPERATING CONDITIONS

The operating conditions for the baths listed in Table 1 are shown in Table 2. Undoubtedly bath (b) can also be operated at elevated

TABLE 2. OPERATING CONDITIONS OF COBALT BATHS

Bath	Current Density, amp/sq ft	Temperature	pH, electrometric
(a)	4-39	Room	5.5+ (est.)
(b)	35-163	Room	5- (est.)
(c)	28-47	Room and up	5.2
(d)	20-140 *	Room and up	...
(e)		Room and up	Slightly acid

* These values depend upon the cobalt content and are still higher at elevated temperatures.

temperature with a corresponding rise in the current density range. The addition of 1.3 oz/gal sulfuric acid or an equivalent amount of 0.2 N hydrochloric or hydrofluoric acid to bath (a) had a tendency to decrease the porosity of the coatings.⁹ The effect of low pH operation on the efficiency of this bath is not stated.

The high current densities indicated in Table 2 are most striking. Contrast them with the much lower values which can be used in nickel plating. A possible explanation is that $\text{Co}(\text{OH})_2$ is precipitated at a

higher *pH* than $\text{Ni}(\text{OH})_2$, namely at 6.81 against 6.66 from 0.05 *N* chloride solutions.¹⁸ Data indicate that, in the recommended *pH* range values, cathode current efficiencies between 90 and 100% are to be expected. Kalmus and associates⁶ frequently stated that the throwing power of the cobalt baths is excellent, but no quantitative data are available.

MAINTENANCE AND CONTROL

The methods recommended for physical and chemical control of nickel solutions are equally applicable to cobalt solutions, except that cobalt cannot be determined by the standard cyanide method. Evans¹⁹ describes a suitable modification.

Kalmus⁶ compared the behavior of the cast and the rolled anodes and commented: "Cast anodes of both nickel and cobalt go into solution much more readily than the rolled anodes. With a number of each in a nickel or cobalt solution the proportion between the two may be so chosen that the composition of the electrolyte remains constant as the anode goes into solution, thus the greater solubility of cobalt anodes . . . as compared with nickel anodes . . . renders the use of a larger proportion of rolled anodes possible in the case of cobalt. . . ."

Regarding cobalt anode composition, Kalmus states: "The greater solution tension of cobalt in the plating baths, as compared with nickel, renders practicable the use of lesser amounts of iron, or no iron at all. Very pure cobalt anodes were readily dissolved in the solution under the conditions of many of our best plating tests." It should be noted here that Kalmus has reference to solutions with little or no chloride as compared with the quantities used in modern nickel plating baths.

Georgi studies the anodic behavior of cobalt²⁰ and nickel²¹ and confirms the difference between the two metals. Thus in 1.0 *N* solutions of sodium sulfate at 20°C pure electrolytic cobalt (0.51% Ni, 0.04% Cu) dissolved with 100% efficiency at current densities as high as 186 amp/sq ft, whereas pure nickel (<0.045% Co, <0.05% Cu, <0.05% Fe) did not dissolve at all at any current density unless the *pH* of the solution was brought down to 3.0 or below.

PREPARATION OF BASIS METALS AND FINISHING OF DEPOSITS

The methods used in preparation of basis metals and finishing after plating in nickel plating are satisfactory also for cobalt plating.

TESTS OF DEPOSITS

Kalmus and associates⁶ have claimed that cobalt provides four times the protection afforded by nickel, but their conclusions have not been substantiated. Fink and Lah²² support Kalmus' observation regarding the superior hardness of cobalt deposits, finding the width of the scratch hardness micro-cuts to be 20 and 34 μ respectively at 205-g (0.45-lb) loads on cobalt and nickel plates from comparable solutions. However, their corrosion tests, which consisted of alternate immersion in 2% sodium chloride solution for 300 hr (15 min wetting, 15 min drying), showed the cobalt specimens losing 0.311 mg/sq cm while the nickel specimens lost 0.264 mg/sq cm. Cobalt is slightly higher in the electromotive series than nickel: -0.30 v as against -0.23 v for nickel at 25°C;²³ and its lower oxides are more easily soluble in dilute acids.

8.

Copper

Copper is deposited from cyanide baths for a number of important applications. Deposition from low concentration striking baths is employed as a cleaning step; it gives a thin film of copper which many believe to improve the adhesion and protective value of subsequent electrodeposits. Heavier cyanide copper deposits are used extensively to prevent casehardening of specified areas of ferrous metal surfaces. Cyanide copper deposits, when used as an undercoat for nickel-chromium coatings, represent a substantial part of the total thickness specified. Another objective of cyanide copper when applied as an undercoat, especially on zinc or zinc-base die castings, is to prevent deposition by immersion in subsequent plating baths. Finally, thin coatings of copper from cyanide baths are used for oxidized finishes and other finishes, or as a protective metal over silvered glass reflectors.

Copper is used on steel as an undercoat to effect savings in polishing and buffing costs, and as a means of improving metal distribution over irregularly shaped articles, by virtue of its superior throwing power, especially in conjunction with periodic reversal of the direct current.* During World War II, and during the Korean emergency, copper was used as a substitute for a substantial part of the total specified thickness of nickel, which was less available. Electrodeposition of copper from acid baths is extensively used for electroforming and electro-refining and to a lesser extent for electroplating. The pyrophosphate-type electrolyte introduced in 1941 is also used in copper plating.

ROCHELLE COPPER

A. KENNETH GRAHAM † AND HAROLD J. READ ‡

Before 1915 copper cyanide baths were invariably made by dissolving copper carbonate in alkali cyanide. The use of tartrates is

* See Reference 19 on page 212

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‡ The Pennsylvania State College, State College, Pa.

mentioned in very early references,^{1,2,*} but their value was apparently not fully recognized other than in a combination cleaning and plating bath mentioned by Watts.³ No chemical control of the bath ingredients was employed, and low current densities and low temperatures were generally used. Deposits from these early baths were, therefore, relatively thin. They were used as a base for oxidized finish or other finishes.

Since 1915 combination alkali cleaning and copper plating baths have not enjoyed any extensive use, chiefly because of the difficulty of control and the demand for better quality. Instead, copper cyanide baths of low metal and high free cyanide content have been used for striking work with copper. Such baths have some incidental cleaning action and are favored by many as a precautionary step in the cleaning cycle.

Heavier copper coatings are now generally used as an undercoat for nickel and chromium on zinc-base die castings,⁴ and quite frequently on ferrous metals.⁵ The initial effort in this direction was limited to thin coatings of cyanide copper or to flash copper deposits from the cyanide bath followed by heavier deposits from the acid copper bath, the latter being operated at a faster plating rate. Because of the demand for heavier deposits at faster plating rates from a bath with throwing power superior to acid copper, the higher concentration copper cyanide bath with relatively low free cyanide was employed.^{6,7}

TABLE 1. CLASSIFICATION OF CYANIDE COPPER BATHS

Bath	Cleaner	Regular Cyanide	Rochelle Type	High Concentration, High Speed
Purpose	Cleaning, striking	Incidental cleaning, striking, plating	Incidental cleaning, striking, plating	Plating
Rochelle salt added	Sometimes	None	Always	None
In use today	Occasionally	Extensively	Extensively	Extensively

It was thus possible to use higher temperatures and current densities, and to obtain heavier deposits and higher efficiencies. The types of copper cyanide plating baths are classified in Table 1.

* References for this portion of the chapter will be found on pages 212 and 213.

With the use of higher current densities and lower free cyanide, difficulty was experienced at the anodes. McCullough and Gilchrist⁸ recommended the use of rochelle salt as a means of improving the anode performance. Unfortunately, they used a very low metal concentration with practically no free cyanide, and even with rochelle salt present the bath employed by them was not entirely satisfactory. It remained for others to combine the advantages of their rochelle salt bath and Pan's higher copper concentration bath to give the practical bath of the rochelle type used in recent years.

Copper, when uniformly deposited, has the property of retarding carbon penetration into a steel base in casehardening operations. Penetration of carbon was found to be a function of both the time and the temperature of treatment⁹ as well as the thickness and porosity¹⁰ of the copper coating. A thickness of 0.0005 to 0.001 in. and greater of copper is employed to protect parts of steel surfaces during casehardening where the carbon enters only the unplated steel surfaces.

To enhance further the brightness and fine-grained structure of the deposit from the rochelle type of bath, lead has been added with some marked success as a grain-refining and brightening agent.¹¹ Caldwell states that the adhesion of nickel deposited over a lead-brightened copper deposit may be poor, but he recommends the following conditions for the most effective use of lead:

1. High cathode current density, 60 to 70 amp/sq ft.
2. A low copper cyanide concentration, 2.4 to 2.6 oz/gal.
3. High pH, 12.6 to 12.8 (colorimetric).
4. High temperature, 71° to 77°C.
5. Low free sodium cyanide concentration, 0.5 to 0.7 oz/gal.

Francis-Carter has reported¹² instances of English practice in the plating of zinc-base die castings at 60 to 80 amp/sq ft, where the tendency of the anodes to polarize has been overcome by careful control of the alkali content of the bath. A pH of 11.6 to 12.3 was recommended for operation at 60° to 70°C. The only difficulty encountered in depositing 0.001 in. (0.0254 mm) of copper in 10 min was the necessity of providing a fume exhaust system to deal with the heavy gas evolution. In American practice a minimum copper thickness of 0.0003 in. (0.0076 mm) is most commonly employed. The conditions are chosen to give a copper deposit of sufficient luster to permit the use of bright nickel and chromium without any buffing. It is doubtful that it is possible to operate as recommended above and still attain the results desired in American practice.

Rochelle copper plating baths are used in depositing for casehardening and in barrel plating operations. The demand for bright copper as an undercoat for bright nickel-chromium deposits, especially on zinc-base die castings, has resulted in the increased use of proprietary brighteners in cyanide copper baths and bright cyanide copper processes, with or without rochelle salt. Copper striking baths are also being operated both with and without rochelle salt.

The value of copper as an undercoat for nickel-chromium deposits over ferrous-base metals is subject to some uncertainty. Exposure tests^{13, 14} on low carbon cold-rolled steel have shown that, with deposits 0.001 and 0.002 in. (0.0254 and 0.050 mm) in thickness, the protective value is higher for a nickel-chromium deposit than when a copper underecoat replaces a portion of the total coating thickness. For a thinner coating the presence of copper as an underecoat is less satisfactory. Outdoor exposure tests* of 0.001 and 0.002 in. (0.0254 and 0.050 mm) nickel-chromium deposits, with and without a copper underecoat, over high carbon steel of bumper quality indicate that the protective value is dependent almost wholly upon the thickness of the nickel coating. A copper strike of the order of 0.0001 in. (0.00254 mm), however, is regarded by some to give better protection than with nickel applied directly to the steel. When completed, the above-mentioned tests should give valuable information on this point.

BATH CONSTITUENTS

The types of rochelle-cyanide copper plating baths in current successful use¹⁵⁻¹⁸ are shown in Table 2.

Bath 1 is frequently used as a strike prior to acid copper or nickel plating and is favored by many as a precautionary step in the plating cycle. It is usually operated at a low temperature and a low current density and at relatively low current efficiency. In actual practice there is no uniformity as to favored bath composition and operating conditions.

With bath 2 heavier deposits with satisfactory properties are possible at higher current densities and high current efficiencies. These advantages are attained without excessive bath decomposition and associated difficulties in anode performance by employing higher operating temperatures, control of pH, higher metal concentration, and substantial amounts of rochelle salt. Metal distribution and throwing

* Based upon early observations of A.S.T.M. test panels by A. K. Graham.

TABLE 2. TYPES OF ROCHELLE-CYANIDE COPPER PLATING BATHS

	Bath Number					
	1		Typical		2	
	oz/gal	g/l	oz/gal	g/l	oz/gal	g/l
CuCN	2.0	15	3.5	26	2.5-6	19-45
NaCN	3.0	23	4.6	35	3.5-7	26-53
Na ₂ CO ₃	Variable		4.0	30	2-8	15-60
Rochelle salt (KNaC ₄ H ₄ O ₆ ·4H ₂ O)	Not generally		6.0	45	4-8	30-60
Cu	1.4	11	2.5	19	2-4	15-30
Free NaCN	0.8	6	0.75	5.6	0.5-1	3-8-7.5
NaOH to give pH	Variable		12.6		12.2-12.8	

power with bath 2 are superior to those attainable with cyanide copper baths operating at 100% efficiency.

A tendency to develop roughness and difficultly buffed deposits with increasing weights of coating is a limitation common to all copper cyanide baths. The maximum thickness of satisfactory plate attainable will depend on the character of deposit desired and the extent to which roughness can be avoided by methods of operation and control.

Periodic reversal of the direct current during electrodeposition has been reported to improve the luster, smoothness, and distribution of copper deposits.¹⁹ There is some indication that the internal stress of the deposit may also be affected.²⁰ Since the proportion of cathodic to anodic components in the cycle chosen influence the results, there are too few data available to draw general conclusions at present.

FUNCTION OF CONSTITUENTS OF BATH

In the rochelle-cyanide copper bath, metal ions are furnished indirectly from complex cyanide anions formed with the alkali cyanide employed. It is generally believed²¹⁻²³ that most of the metal exists in the form of the tricomplex $[\text{Cu}(\text{CN})_3]^-$, although the di- and tetra-complexes, $[\text{Cu}(\text{CN})_2^-]$ and $[\text{Cu}(\text{CN})_4]^-$, are known to exist.²⁴ Conductivity of the bath is increased by increasing both the uncom-

bined alkali cyanide and the concentration of the copper complexes.^{7, 25} In the latter case, equilibrium shifts to lower complexes occurring with increased temperature probably liberate free cyanide.^{15, 16, 21, 25} The caustic alkali that is used to increase the *pH* of the bath also increases the conductivity. Sodium carbonate, however, contributes little, if anything, to the conductivity of the bath, but exerts a strong buffer action at a *pH* of about 10.3 (colorimetric).^{15, 26} Trisodium phosphate has also been mentioned as an addition,²⁶ and, when present in small amounts, it will buffer the bath below a *pH* of about 12.2 (colorimetric). At *pH* values above 12.2 there is sufficient alkali reserve to give the equivalent of a buffered solution.

Rochelle salt may form temporary complexes with copper by reacting with products of electrolysis in the anode film. By its use a lower concentration of free cyanide may be employed without impairing anode corrosion, and higher current densities and efficiencies are attained.^{15, 16} Improvement at the cathode resulting from the use of rochelle salt is associated in part with the formation of complexes with basic salts which may be present. Smith and Munton²⁷ have shown that the substitution of sodium potassium citrate for rochelle salts in an otherwise typical bath enhances the physical qualities of the deposit, but decreases both the cathode and anode efficiencies, the latter to a considerable extent. The tendency toward excessive anode polarization is more marked in the citrate solutions. The potassium content of the bath in the presence of the citrate ion has a decided and somewhat complex effect on electrode efficiencies.

Sodium sulfite and bisulfite have been recommended as additions to copper cyanide baths. The effect of sulfites, together with thiosulfate, is somewhat obscure. It is known, however, that both may improve the brightness of the deposit. This may result from the formation of sulfur complexes to which the cyanide copper bath is known to respond. Unfortunately, the higher current density and temperature usually employed with the rochelle copper bath cause decomposition of these complexes and precipitation of metal sulfides which have been found to cause serious roughness, anode films, and irregular deposits. It may also be that the formation of metal sulfides results in purification of the bath with respect to some foreign metal ions, thus improving luster in a manner similar to that involved when sodium sulfide is used in zinc cyanide plating baths.

Lead in the form of sodium plumbite has been added as a brightener and more particularly as a means to produce a finer-grained deposit prior to bright nickel and chromium.¹¹ Lead is codeposited with the copper and must be added at regular intervals if uniform results are

to be obtained. The amount of lead required to give optimum results may vary from 0.002 to 0.004 oz/gal. The agitation, temperature, current density, and bath concentration will influence the amount to be employed. Chemical control of lead concentration in the bath is not simple, and the successful use of lead depends largely on the experience of the operator. Baths with the lower lead content give brighter deposits but lower efficiencies at both anode and cathode. For uniform results the free cyanide must be closely controlled within the indicated limits by frequent analyses. It has been reported that the addition of 2 and 75 ppm of lead, as lead acetate, to a similar type of bath produces contractile stresses in the deposit of 11,300 and 15,400 lb/sq in. respectively.²⁰

The use of certain betaines²⁵ or of thiocyanates plus sucrose²⁹ as addition agents for the copper cyanide baths has been patented.

Rochelle salt concentration of about 6 oz/gal is usual. Wagner and Beekwith¹⁶ showed that the optimum concentration was about 3 oz/gal, somewhat lower efficiencies being obtained at higher values. Since this constituent is lost chiefly by drag-out, the analyses should be frequent enough to maintain the concentration within the desired limits. A higher average concentration requires less frequent analyses.

A definite concentration of carbonate must be present to reduce anode polarization, to improve pH control, and to prevent attack of iron anodes, etc.^{15, 26} In practice the carbonate concentration is sometimes allowed to reach about 18 oz/gal when the excess is removed by freezing, or the entire bath is discarded. Wherever refrigeration equipment is available, it is preferable to maintain the carbonate concentration below 13.3 oz/gal.

OPERATING CONDITIONS AND CHARACTERISTICS OF THE ROCHELLE-CYANIDE BATH

A cathode current density as high as 70 amp/sq ft is used in practice. Ordinarily, the brightest deposits are obtained between 18.6 and 56 amp/sq ft, depending upon the temperature and agitation employed.^{15, 17, 18}

The anode current density must be carefully controlled. A safe recommendation would be to have an anode area at least equal to twice the cathode area. Iron anodes equivalent to about 5% of the total area have been suggested.¹⁵ The current density at the anode, therefore, is always considerably less than at the cathode.

A temperature of 50° to 80°C is employed. The higher the temperature, the more rapid will be the decomposition of free cyanide and

the formation of carbonates. Higher temperatures also give higher efficiencies at both anode and cathode. A temperature between 55° and 70°C is favored by many.^{15, 17}

A pH within the limits 12.2 to 12.8 will give good results.¹⁵ The lower value will be more difficult to maintain because of the poor buffer characteristics of the bath. In practice, a pH between 12.5 and 12.8 is usually employed. Too high a pH must be avoided as the anode efficiency may be prohibitively low. Maher³⁰ reports the elimination of blistering of plated zinc-base die castings when subjected to heat by lowering the pH from the range 12.2 to 12.6 to about 9.4 when plating from a rochelle bath containing 0.8 g/l Na₂S₂O₃.

The average bath composition mentioned above will give cathode efficiencies between 60 and 30% at 55°C and between 70 and 40% at 70°C when operated at current densities of 18.6 and 56 amp/sq ft without agitation.¹⁵ Agitation will raise these values somewhat.

The anode efficiency for the same bath will be 50 to 70% at current densities approximately half of those mentioned above.¹⁵ Agitation and higher temperatures will raise the anode efficiency.

Most published data on throwing power of the cyanide bath are limited to current densities under 9.3 amp/sq ft. At the higher current densities and temperatures employed in rochelle copper plating, the magnitude of the effect of factors influencing throwing power may be quite different. The greatest single factor influencing throwing power and metal distribution appears to be the variation in cathode efficiency with current density. For this reason baths which operate at 100% or nearly constant cathode efficiency within the current density range involved are more limited in application, in that an excess of metal will be deposited on the high current density points before the minimum desired thickness is obtained in the recesses or low current density points. In other words, lowering cathode efficiency by increasing the hydrogen evolution will increase the throwing power.

The degree of agitation will vary greatly in different installations. Wherever possible, the degree of agitation is determined together with a consideration of the other variables affecting the character of the deposit. Agitation results in higher efficiencies, more uniform bath composition, more uniform anode corrosion, and an increase in the current densities at which the brightest deposits are obtained.¹⁵

Although numerous investigations of polarization phenomena have been made in copper cyanide solutions, only anode polarization has so far been studied in the rochelle cyanide salt bath. Graham and Read^{15, 25} have studied the influence of bath composition, pH, and

current density on anodic polarization for both copper and copper-iron anodes at 55°C. In general, the polarization curves exhibit two points of inflection which have been identified with the cuprous and cupric reactions at the anode. The effect of bath variables on these reactions has been discussed.²⁵ The most interesting information which may be found in a study of anodic polarization defines, for a given set of bath conditions, the limiting current density beyond which excessive polarization occurs.²⁵ Excessive polarization causes insulation of the anode and usually necessitates the removal of the anodes for cleaning. Variations in metal content and free cyanide have little effect on the limiting current density. If the carbonate content is high, the copper may act as an insoluble anode and excessive polarization does not occur. Changing the pH from 10.3 to 12.8 does not greatly affect the limiting current density, but at a pH of 13.3 the anode does not polarize excessively if carbonates are present (the efficiency, however, drops to a very low value). The presence of tartrates does not overcome the tendency of the anode to polarize excessively, although the allowable current density is raised when both carbonates and tartrates are present. If insoluble iron anodes are used along with copper anodes, higher anode current densities may be used because the iron tends in effect to depolarize the copper.

MAINTENANCE AND CONTROL

Filtration of the rochelle salt bath is becoming more common. Smoother, more uniform, brighter deposits may frequently result. Of the available filter media, paper backed with a fairly open cloth or heavy paper disks are the most satisfactory. The use of filter aid is losing favor because of possible silica contamination of the bath.

The best way to deal with impurities is to prevent them from entering the bath. Proper pH control and the presence of a minimum concentration of carbonate will prevent excessive contamination from iron.¹⁵ Iron has been shown to reduce current efficiency¹⁶ and unfortunately cannot readily be removed from the bath.

It has been reported²¹ that 0.00134 oz/gal of Cr⁺⁶ lowers the cathodic efficiency in a cyanide copper bath and that the efficiency will be reduced to zero by 0.0134 oz/gal Cr⁺⁶. A slight excess of sodium hydrosulfite, Na₂S₂O₄, added to the bath reduces the Cr⁺⁶ to Cr⁺³. Cr⁺³ precipitates as hydroxide or will form a complex with rochelle salt if present. In the latter case, Cr⁺³ may be reoxidized to Cr⁺⁶ at the anode, so that periodic additions of the sodium hydro-

sulfite must be made. A few grams excess of sodium hydrosulfite has no harmful effect at the cathode.

Zinc resulting from die castings allowed to remain in the tank can be removed by electrolyzing at room temperature at that current density which gives the most brassy or off-color deposit. This is usually at 2 or 3 amp/sq ft. Sodium sulfide may be used to precipitate zinc, but an excess will cause irregular results.

Activated carbon is sometimes used to advantage, particularly if organic contamination of the bath has occurred.

Hellige color disks or pH sets equipped with color tube standards and comparator block are most satisfactory for controlling pH. La Motte violet indicator has been successfully used by many. It has been found that pH papers are unreliable with this bath. Thompson³² has indicated the magnitude of the salt errors involved.

Hull cell plates³³ or bent cathode tests³⁴ are of value only in so far as they are correlated with the bath variables and operating conditions by the individual operator. If intelligently used, such tests are of real value. This is particularly true of the Hull cell plates when they are used to observe the bright plating current density range of a bath under definite operating conditions.

ANALYTICAL METHODS

COPPER

The copper content of the bath is usually determined as follows:

1. Put a 5-ml sample of the bath, using a sampling burette, into a 250-ml Erlenmeyer flask.
2. Put 5 ml of concentrated nitric acid into a 50-ml graduate, and then cautiously add 5 ml of concentrated sulfuric acid. Pour this acid mixture into the Erlenmeyer flask under a well-ventilated hood and shake. Boil until dense white fumes are evolved.
3. Cool and add 100 ml of distilled water, then warm until thoroughly dissolved.
4. Cool and add concentrated ammonium hydroxide while shaking until a deep blue color appears. Then boil for about 15 min to remove excess ammonia.
5. Add 10 ml acetic acid (30% by volume) and a pinch of sodium fluoride, sufficient to combine with any iron. Boil to redissolve any copper compounds. The solution should now be clear and blue.
6. Cool to room temperature, add 15 ml of 30% potassium iodide solution and shake.

7. Titrate immediately, using sodium thiosulfate solution (approximately 25 g/l $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 1.0 g/l of sodium hydroxide standardized * against pure copper) until the brown color begins to fade.

8. Add 2 ml of 1% starch solution (1 g made into a paste with cold water and then added to 100 ml of boiling water, cooled and decanted). Continue the titration until the blue color entirely disappears, even after standing 1 min.

9. The milliliters of the standard solution required multiplied by the factor ($1.69 \times$ normality of thiosulfate) gives the ounces per gallon of copper in the bath.

FREE SODIUM CYANIDE

Free or uncombined sodium cyanide is analyzed as follows:

1. Cool sample to *room temperature* and measure 10 ml with a sampling burette into a 250-ml Erlenmeyer flask.

2. Add 100 ml of distilled water.

3. Add 5 ml of a 10% potassium iodide solution.

4. Titrate with a 0.1 N silver nitrate solution (17.0 g/l) until a permanent turbidity is obtained.

5. The volume of the standard silver solution multiplied by the factor 0.1313 gives the ounces per gallon of free sodium cyanide in the bath.

CARBONATE

Carbonates are determined in order to find out when to discard the bath or when to chill the bath for carbonate removal. The method is as follows:

1. Place a 10-ml sample of the bath into a 250-ml beaker.

2. Add 100 ml of distilled water and warm.

3. Add 10% barium nitrate solution while stirring until no more precipitate forms. Allow to settle.

4. Filter, adding a few drops of the barium solution to the filtrate to be sure precipitation has been complete, then wash with hot water.

5. Transfer the filter paper and precipitate to the beaker in which the precipitation was made.

* To standardize the thiosulfate solution, about 0.20 g of pure copper wire or turnings is accurately weighed, transferred to a 250-ml Erlenmeyer flask, and dissolved with 10 ml of 1:1 nitric acid. Then add 5 ml of concentrated sulfuric acid and heat until heavy white fumes are evolved. Cool and proceed as outlined above from 3 to 8. The weight of the copper sample divided by the milliliters of thiosulfate solution used and multiplied by 15.73 gives the normality of the thiosulfate.

6. Add 50 ml of distilled water and a few drops of 0.2% methyl orange solution.

7. Titrate with a 1.0 *N* hydrochloric acid solution until a permanent pink color is obtained.

8. The milliliters of standard acid used multiplied by the factor ($0.705 \times$ normality of acid) gives the ounces per gallon of sodium carbonate in the bath.

ROCHELLE SALT

The rochelle salt concentration must be determined periodically, and the method of Stoddard³⁵ as outlined below is recommended:

1. Into a 250-ml volumetric flask, measure exactly 2 ml of the plating solution.

2. Add 100 ml of distilled water.

3. Add a particle of *solid* phenolphthalein about the size of a pin head.

4. Add dilute sulfuric acid, about 0.1 *N*, until the pink color of the phenolphthalein indicator disappears.

5. Add exactly 5 ml of nitrobenzene (poison).

6. Add dropwise, with constant shaking, a 10% solution of silver nitrate. The endpoint for the silver nitrate addition may be observed when the color of the precipitate changes from white to blue-gray. The silver nitrate removes all the materials which would ordinarily interfere with the subsequent steps.

7. Shake the flask for half a minute or until the precipitate is entirely coagulated by the nitrobenzene. Add a drop of silver nitrate to make sure an excess is present.

8. Add distilled water, making the solution up to the 250-ml mark.

9. Add exactly 5 ml of distilled water. This extra distilled water makes up for the 5 ml of nitrobenzene which was added earlier and which does not dissolve in the aqueous solution.

10. Shake the flask well to insure thorough mixing. The solution should now be clean and colorless while the nitrobenzene and the precipitate are present in the bottom of the flask in a dark-colored mass.

11. Draw out exactly 50 ml of this solution for the permanganate oxidation.

12. Run this 50-ml sample into a 500-ml Erlenmeyer flask. (It is advisable to run check samples until the following procedure has been mastered, and afterward whenever accurate results are required.)

13. To the sample add 5 ml of 20% sulfuric acid, 5 g of manganous sulfate, and 100 ml of distilled water.

14. Heat the sample to 70°C and add slowly with agitation exactly 20 ml of 0.1 N potassium permanganate.
15. Allow the hot sample to stand for a few minutes and then cool it to room temperature under running water.
16. Add 2 g of c.p. potassium iodide. Shake the flask for 2 or 3 sec and then titrate with 0.1 N sodium thiosulfate, using a starch solution indicator.
17. Subtract the number of milliliters of 0.1 N thiosulfate used from the number of milliliters of potassium permanganate, calculated as 0.1 N, originally added. This difference when multiplied by 0.0047 gives the weight of the tartrate as sodium potassium tartrate, or rochelle salt, in the 50-ml sample. Multiplying this result by 5 gives the weight of rochelle salt in 2 cc of the plating solution. Multiplying this result by 500 gives the number of grams per liter of rochelle salt. In other words, multiplying the number of milliliters of 0.1 N permanganate required for a 50-ml sample by the factor 11.75 gives the number of grams per liter of rochelle salt. If the result is to be expressed in ounces per gallon, the cubic centimeters of permanganate required should be multiplied by 1.57

BATH pH

If pH is correlated with respect to the caustic soda concentration of the bath, the following titration method of pH control may be used:

1. Measure a 10-ml sample of the bath into a 250-ml Erlenmeyer flask.
2. Add 10 ml of distilled water and cool to *room temperature*.
3. Add 0.5 ml of La Motte sulfo-orange indicator and titrate with 0.5 N acid (hydrochloric or sulfuric) to a yellow color.
4. The endpoint is reached so gradually that more accurate control is possible by using a separate flask containing 10 ml of a 20% sodium carbonate solution, 0.5 ml of sulfo-orange indicator, and sufficient distilled water to equal the volume of the sample being titrated, as the color to match for an endpoint.
5. The concentration of caustic soda in ounces per gallon equals the milliliters of acid used multiplied by the factor ($0.268 \times$ normality of acid). This is not the exact concentration of caustic but, if the relation of the optimum pH of the bath to the caustic value is once established, the method gives a very satisfactory control.

Control of pH by the titration method mentioned above has the advantage of indicating directly the approximate quantity of caustic present above the sulfo-orange sodium carbonate endpoint. The pH at this endpoint corresponds to 11.5, or that of sodium carbonate in

water. Approximately 0.75 g./l. of caustic soda will raise the *pH* from this value to 12.7. For other *pH* values the buffer curve mentioned below may be used in making adjustments.

When colorimetric *pH* measurements are employed, the buffer curve in Fig. 1 also proves very useful.²⁶ The approximate concentration of caustic soda or concentrated sulfuric acid required to change the *pH* of any rochelle salt cyanide copper bath is indicated. Should it

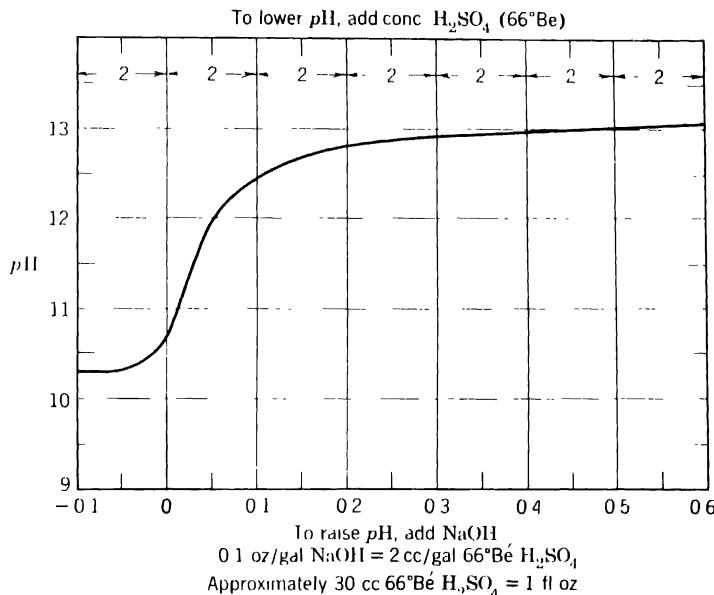


Fig. 1. Buffer curve for rochelle copper plating bath

become necessary to lower the *pH* by the addition of acid, it is recommended that the acid be diluted with about two parts by volume of water (*add the acid to the water*) and then added through a tube well below the surface of the bath with vigorous stirring.

ANODES

Cast ball, cast elliptical, or electrolytic copper anodes are used. The latter two may be used together with a small steel anode area (about 5%) as a safeguard against excessive polarization,^{15, 25} and as a partial means of regulating the metal content of the bath. If the anode current density is kept below the critical value at which excessive polarization occurs,²⁷ the corrosion products formed at the anodes are soluble in the bath with good efficiency. Above the critical

current density value the efficiency approaches zero. The anode efficiency may also approach zero, without excessive polarization at high current densities, if the carbonate concentration is high. If a heavy insulating film forms on the anode as the result of excessive anode current density, the anodes must be removed from the bath and cleaned. The film that forms under proper current conditions is soluble. Solution agitation at the anode raises the allowable anode current density and increases the anode efficiency, but may cause roughness if excessive.

Uncombined cyanide, whether it is added as such or results from an equilibrium shift from higher to lower copper cyanide complexes with increasing temperature, furnishes the $(CN)^-$ ions controlling anode corrosion.^{16, 16, 21} The tartrate ion contributes to anode corrosion, although the manner in which it functions is not clear.^{21, 27}

PREPARATION OF THE BASIS METALS

Zinc-base die castings are usually cast under such conditions as to reduce to a minimum any polishing or buffing. By so doing, the fine-grained structure of the chilled skin surface is preserved. In a summary of commercial practice, Anderson¹⁷ indicates that there is considerable variation in the polishing and buffing treatment. In general, the parting lines are always removed by polishing. In this process the entire surface is frequently polished. The polishing grain size and number of steps vary widely. A "180 grain" followed by a "220 grease" operation is general practice. Sheepskin, felt, and cloth wheels are used.

In many cases no color buffing is done. When the die castings are color buffed, tripoli or a combination of tripoli and lime for a cut and color operation is employed, either loose or stitched buffs being used.

The cleaning of die castings involves degreasing with solvents, emulsion-type cleaners, or immersion alkaline baths, and mild electrocleaning followed by a mild acid etch prior to plating.^{17, 17, 19} The electrocleaning, regardless of whether it is anodic⁴⁰ or cathodic⁴¹ and irrespective of the particular acid employed, must be sufficiently mild to preserve the finish and to give no staining. The cathodic procedure is more likely to cause staining of a permanent nature, whereas any stain from anodic treatment can be dissolved.

Ferrous metals are given various polishing, buffing, and cleaning treatments depending upon whether one is dealing with cast or malleable iron, low or high carbon steel, cold-rolled stampings, or hot forgings. The nature of the contamination, whether a drawing com-

pound, lubricant, polishing composition, or oxide, determines the required cleaning treatment. Obviously, there cannot be the uniformity of treatment that exists with zinc-base die castings. Therefore no attempt will be made to discuss these treatments other than to point out that satisfactory results depend upon freedom from films and solid matter on the surface to be copper-plated, and the better the luster and finish as the work enters the copper bath, the smoother, brighter and more uniform will be the deposit.

Meyer⁴² recommends plating copper from a low pH cyanide bath directly on a treated aluminum surface. If the aluminum has been buffed, it must be precleaned before it is given the following treatment. The parts are first cleaned in an alkali cleaning solution. The smut, which may contain iron, copper, manganese, nickel, or magnesium oxide, is removed in a solution 2 parts nitric acid and 1 part water by volume. To remove a smut containing silicon, a mixture of 3 volumes of concentrated nitric acid to 1 volume 50% hydrofluoric acid is recommended. The subsequent rinse should be at room temperature. The parts are then immersed in a zincate solution containing 7.4 to 9.4 oz/gal of sodium hydroxide at 20° to 70°C. The parts should preferably be agitated initially to remove the water film. The treatment time varies for different alloys. An aluminum-silicon alloy requires 5 to 10 sec, pure aluminum requires about 10 sec, and aluminum-copper alloy requires 1 min or more immersion time. The recommended conditions for copper plating were 26.5° to 32°C, a free cyanide concentration below 0.4 oz/gal, and a pH below 10.5. An initial current density of 10 to 30 amp/sq ft for 1 min is followed by a normal value.

A patent⁴³ has been granted which covers the use of the following dipping solution for the preparatory treatment of aluminum:

Water	1 gal	1 l
Caustic soda	53.5 oz	400 g
Zinc oxide	10.7 oz	80 g
Copper (e.g., in form of potassium-copper cyanide)	0.27 oz	2 g
Sodium sulfite	3.34 oz	25 g

TEST OF DEPOSITS

The thicknesses of copper deposits now employed in composite coatings on steel and zinc base die castings are illustrated in Table 3. It is interesting to note that copper represents from 40 to 60% of the total

TABLE 3. SPECIFIED THICKNESS OF COPPER FOR Cu-Ni-Cr COATINGS

On Steel							
Total Thickness, †	minimum	Copper Thickness,	minimum	Allowable Copper Using Minimum Nickel			
in.	mm	in.	mm	% total min			
0.002	0.0508	0.001	0.0254	50			
0.00125	0.0318	0.00065	0.0165	52			
0.00075	0.0190	0.00035	0.0089	47			
0.0004	0.0102	0.0002	0.0051	50			

On Zinc-Base Die Castings							
Total Thickness, †	minimum	Copper Thickness,	minimum	Allowable Copper Using Minimum Nickel			
in.	mm	in.	mm	total min			
0.00125	0.0318	0.0004	0.0102	60			
0.00075	0.0190	0.0003	0.0076	60			
0.0005	0.0127	0.0002	0.0051	40			

* For complete specification data, consult A.S.T.M. Tentative Specifications A166-45T and B142-45T (1946) for steel- and zinc-base die castings respectively.

† Heavier coatings for more severe service.

minimum thickness specified. For the heavier coatings greater thicknesses of copper and less nickel may be used should the latter become less available.

The microscopic method of determining thickness⁴⁴ is most commonly recommended. The Amineo-Brenner Magne-Gage⁴⁵ may also be employed to advantage for copper deposits on iron or steel.

The Hull-Strausser test⁴⁶ has been developed for determining the local thickness of copper. The following solution is recommended for this purpose: ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 60.3 oz/gal; antimony oxide (Sb_2O_3), 2.7 oz/gal; hydrochloric acid (conc. c.p. 1.19 sp. gr.), 200 ml/l; glacial acetic acid (CH_3COOH), 250 ml/l.

On copper-plated steel the endpoint is a bright clean spot contrasting with the copper, but over zinc the endpoint is a dull black spot which shows in contrast with the copper. The thickness of the deposit is calculated by using the stripping factor of 20 sec./0.0001 in. of copper. An accuracy of $\pm 10\%$ can be obtained for thicknesses varying between 0.0001 and 0.0062 in. (0.0025 mm to 0.157 mm). It is claimed that results closer to the true thickness can be obtained by maintaining the temperature at or near 24°C and regulating the rate of dropping to 100 drops/min. Ordinarily, the test solution should be kept between 21° and 27°C, and the rate of dropping should be maintained within the prescribed limits of 90 to 110 drops/min to obtain the accuracy claimed above. In testing heavy deposits, of 0.001 in. (0.025 mm) or more, it is recommended that one wipe the area exposed to the solution with a clean cloth at intervals of 30 or 45 sec to facilitate closer determination of the endpoint.

A simple test¹⁷ has been devised to determine whether an adequate thickness of copper has been applied to protect steel against casehardening. This consists in applying to the surface a drop of 1:1 nitric acid and noting the time required before the copper is dissolved and the steel attacked. A drop is allowed to remain on the surface for 9 sec. It is then wiped or blotted, and the process is repeated until a brown stain shows the steel to be exposed. One drop for 9 sec is equivalent to .0001 in. (0.00025 mm) thickness of copper. This thickness will be adequate to protect the surface while casehardening to a depth of 0.002 in. (0.050 mm).

Since rochelle copper deposits are never used as the final coating for severe exposure and, when employed in mild exposures, are usually oxidized or colored and always lacquered, they are seldom, if ever, given accelerated corrosion tests.

Tensile tests of copper electrodeposits have not been required as part of the specifications for plated products. Fundamental data on the relation between hardness, tensile strength, yield strength, per cent elongation and internal stress, and the effect of variations in the plating bath composition and operating conditions remain to be determined.

A method of determining the stress in copper deposits has been reported.²⁰ In this report Graham and Lloyd showed that the stress increased with increase in current density and with the addition of lead (2 to 75 ppm) to the plating bath. As the temperature of the deposition increased, the stress in the deposit decreased. Increasing the copper concentration of the bath decreased the stress in the deposit. The addition of potassium thiocyanate (2 oz/gal) produced an ex-

pansive stress instead of the contractile stress usually observed. The magnitude of the stress values reported varied from 15,400 lb/sq in. (contractile) to 5000 lb/sq in. (expansive).

HIGH EFFICIENCY CYANIDE COPPER

R. R. BAIR* AND D. A. SWALHEIM*

Pan¹,† and others showed that plain, high concentration cyanide copper electrolytes could be operated at moderately high current densities to give high cathodic efficiencies. This work was done at 27°C, and it resulted in dull, rough deposits which were generally unsatisfactory at thicknesses of about 0.001 in. The recent incorporation of alkali, alkali thiocyanate,^{2,3} and specific surface-active agents⁴ permits the deposition of bright, smooth deposits up to 0.002 in. and even 0.005 in. under ideal conditions. These electrolytes may be operated at current densities up to 10 to 35 amp/sq ft by mechanically agitating the work at rates of 4 to 10 ft/min. Higher current densities may be employed if this agitation is augmented through the use of "solution circulation." Current densities in excess of 50 amp/sq ft have been applied successfully in commercial practice by using combinations of agitation and solution circulation to obtain rapid replacement of the electrolyte film at the cathode surface.

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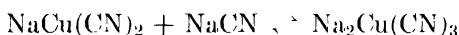
† References for this portion of the chapter will be found on page 225.

The high efficiency cyanide copper plating baths, introduced commercially in 1938, are now being used extensively to produce copper deposits for decorative surfaces, per se, as base coatings under nickel and chromium and as a stop-off layer for selective casehardening. These baths show excellent performance in permitting relatively high rates of deposition under economical conditions of operation. They produce deposits of good brightness and ductility, even in heavy coatings.

Some of the parts are intricate in design and require the high throwing power of the high efficiency baths to obtain sufficient plate thickness for adequate corrosion protection on exposed but recessed areas. The anodic and cathodic current efficiencies are approximately 100%; this gives adequate simplicity of chemical control and maintenance in commercial operation. The installation of diaphragms⁵ in copper plating tanks has overcome most of the difficulties from particle roughness of deposits in the thickness range of 0.001 to 0.002 in. Copper ions are cuprous in the cyanide electrolytes and cupric in the acid baths. Thus, the same amount of current (assuming 100% efficiency) will deposit twice as much copper from the cuprous cyanide bath as it will deposit from the acid or cupric electrolyte. This feature results in substantial economies in the installation and operation of plating power facilities.

FUNCTIONS OF BATH CONSTITUENTS

Copper cyanide is insoluble in water but dissolves in solutions containing alkali metal cyanides to form soluble complexes as indicated by the following equations:^{6,7}



The ratio of sodium and copper cyanides corresponding to $\text{Na}_2\text{Cu}(\text{CN})_3$ is optimum for the high efficiency electrolyte. At a ratio corresponding to $\text{Na}_3\text{Cu}(\text{CN})_4$, hydrogen is evolved at the cathode during electrolysis. The sodium cyanide in excess of $\text{Na}_2\text{Cu}(\text{CN})_3$ is termed "free cyanide." It is this "free cyanide" that controls the very low finite concentration of copper ions. The ionization reaction is rapid, and additional cuprous ions are supplied at the low concentration level to replace those removed by electrolytic reduction and deposition.

The higher the "free cyanide" over that required for the complex $\text{Na}_2\text{Cu}(\text{CN})_3$, the better is the anodic corrosion. Excessive "free cyanide" will lower the cathodic efficiency. This is to be avoided, because a decrease in the cathodic efficiency will cause the production of deposits having inferior quality. Satisfactory deposits may be obtained if no "free cyanide" is present, but anodic corrosion will be poor. The complexes formed by sodium cyanide and potassium cyanide with copper cyanide are quite similar, except that the potassium complexes are somewhat more soluble.

Sodium hydroxide or potassium hydroxide is used in high efficiency copper electrolytes, primarily to improve conductivity. It is important that the conductivity be fairly high to obtain satisfactory throwing power. The alkali hydroxide also improves the quality of the deposits and is a factor in eliminating erratic anodic corrosion.

The thiocyanate functions mainly to give a brighter deposit.² It also improves anodic corrosion and renders the electrolyte more tolerant toward various metallic and organic contaminants. For example, as little as 0.05 oz/gal of zinc metal contamination may cause trouble if no thiocyanate is present in the bath. With the use of thiocyanate, a concentration of 0.3 oz/gal of zinc metal may be tolerated. Deteriorous plating effects due to lead compounds in the bath are also minimized.

Carbonates tend to build up in the electrolyte during operation, because of absorption of carbon dioxide from the air, and by hydrolysis and oxidation of the cyanide radical if the baths are operated under conditions giving polarization films on the anodes. The latter condition should be avoided, since it will result in a rapid deviation from recommended bath compositions. There are no appreciable deleterious plating effects from alkali carbonates in concentrations up to about 10 oz/gal. Higher concentrations will lower the optimum current density range. Carbonates, therefore, must be controlled to realize maximum speed of plating.

Under most commercial plating conditions, the high efficiency copper cyanide electrolytes inherently will show a tendency to produce "pitted" deposits. Pitting usually is produced by hydrogen or air bubbles adhering to the cathode surfaces. Freedom from pitting may be obtained by the addition of certain quaternary ammonium derivatives.⁴ Continuous purification of the electrolytes with activated carbon is used to remove organic contamination. Organic addition agents of the "wetting-agent" type also tend to decrease the sensitivity of the electrolytes to organic contamination. This is significant, particu-

larly in operating large installations in which a reduction of the required frequency for activated carbon purification treatments is desirable.

BATH FORMULATIONS

Sodium cyanide, potassium cyanide, or mixtures of both may be used with copper cyanide (see Table 1). When mixtures are em-

TABLE 1. CYANIDE COPPER BATH FORMULATIONS

	Dil. Plain Cyanide	Rochelle Type	High Conc. (Pan 1)	du Pont K ¹ Formulation	du Pont Na ⁺ Formulation
CuCN	2 oz/gal	3.5 oz/gal	12 oz/gal	8 oz/gal	16 oz/gal
NaCN	3 oz/gal	4.6 oz/gal	14.1 oz/gal		18.6 oz/gal
KCN				12.7 oz/gal	
Na ₂ CO ₃	2-4 oz/gal	4 oz/gal	10.4 oz/gal	None added	None added
NaOH		To pH 12.6			
KOH ³				5.6 oz/gal	
NaCNS ²				0.75 oz/gal	2.0 oz/gal
Surface-active agents ⁴				10 ml/gal	10 ml/gal
Rochelle salt		6 oz/gal			
Temperature	22-24°C (72-75°F)	55-70°C (130-158°F)	22-23°C (72-74°F)	72-78°C (161-172°F)	72-78°C (161-172°F)
Cathode cd	5-12 amp/sq ft	15-60 amp/sq ft	18.5 amp/sq ft	10.40 amp/sq ft	10-40 amp/sq ft
Cathode efficiency	30-60%	30-70%	95%	99%+	99%
Deposit appearance	Dull red	Matte pink	Dull pink	Bright	Bright

ployed, the relative amounts of each may be varied within rather wide limits. The potassium formulation bath is recommended for optimum results, since it is more tolerant to organic contamination and has a greater operating flexibility.

Some compositions are formulated in Table 2 to give comparable operating characteristics. If higher operating current densities are

TABLE 2. BATH FORMULAS FOR STILL PLATING

	Na ⁺ Formulation	Mixed Formulation	K ⁺ Formulation
CuCN	16.0 oz/gal (120.0 g/l)	10.0 oz/gal (75.0 g/l)	8.0 oz/gal (60.0 g/l)
NaCN	18.0 oz/gal (135.0 g/l)	6.1 oz/gal (45.8 g/l)	
KCN		7.7 oz/gal (57.8 g/l)	12.6 oz/gal (94.5 g/l)
NaCNS	2.0 oz/gal (15.0 g/l)	1.3 oz/gal (9.8 g/l)	0.6 oz/gal (4.5 g/l)
NaOH	4.0 oz/gal (30.0 g/l)	2.0 oz/gal (15.0 g/l)	
KOH		2.8 oz/gal (21.0 g/l)	5.6 oz/gal (42.0 g/l)
Anti-pit agent	10 ml/gal	10 ml/gal	10 ml/gal

required, a higher metal content may be used in either the mixed or the potassium formulation. The lower solubility of the sodium salts prevents the use of a higher metal content in the sodium formulation

bath. The bath compositions given may vary $\pm 10\%$ without introducing adverse plating characteristics.

The general operating conditions shown in Table 3 are recommended for still plating.

TABLE 3. OPERATING CONDITIONS FOR STILL PLATING

Cathode current density	10-40 amp sq ft
Anodic current density	10-20
EMF	1-2.5 v
Rate of deposition	528 amp min/sq ft deposits 0.001 in. copper
Cathode efficiency	99%+
Anode efficiency	99%+
Temperature	70-80°C (158-176°F)
Agitation	2-15 ft/min
Anode to cathode area ratio	Approx. 2:1

In barrel plating, electrolyte formulations and operating conditions must be adjusted for the low cathodic and high anodic current densities. The thiocyanate² brightener normally is not used, the caustic content is reduced, and the "free cyanide" is increased. The surface-active agents⁴ are considered impractical because of the foam formed by rotation of the barrel. Bath compositions and operating conditions recommended for barrel plating are given in Table 4.

TABLE 4. BATH COMPOSITIONS AND OPERATING CONDITIONS FOR BARREL PLATING

	Dilute Bath	Cone. Bath
CuCN	8.0 oz/gal (60.0 g/l)	12.0 oz/gal (90.0 g/l)
KCN or NaCN	13.0 oz/gal (97.5 g/l)	19.0 oz/gal (142.5 g/l)
	10.0 oz/gal (75.5 g/l)	14.5 oz/gal (108.8 g/l)
KOH or NaOH	0.7-1.4 oz/gal (5.3-10.5 g/l)	0.7-1.4 oz/gal (5.3-10.5 g/l)
	0.5-1.0 oz/gal	0.5-1.0 oz/gal
pH	12.6 (elect.)	12.6 (elect.)
Temperature	49°C (120°F)	66°C (150°F)
Anodes	Pure copper	Pure copper
EMF	3-4 v	4-5 v

Sodium hyposulfite or lead acetate (0.5 to 1.0 oz/100 gal) may be used as brightener in the barrel plating application of high efficiency baths. The addition of about 0.25 oz/gal/day of sodium bisulfite is beneficial in improving deposit uniformity and smoothness.

OPERATING PROCEDURES

The following discussions are general in nature because local production requirements will determine the actual operating details.

GENERAL PRINCIPLES

Because of the absence of hydrogen evolution there is substantially no cleaning action at the surface of the parts during the plating operation. Cleaning of the parts prior to plating must, therefore, be of the highest quality. Satisfactory results may be obtained through solvent degreasing followed by electrocleaning. If the cleaning is inadequate, the copper plate will be inferior. When inadequate cleaning is used, the bath will require frequent purification treatments to remove organic contaminants.

A copper strike plate about 0.00005 in. thick is applied in a low efficiency, cyanide copper bath prior to plating in the high efficiency electrolytes. This practice is followed because the low "free cyanide" content of the high efficiency bath favors the formation of mechanically unsound immersion deposits when deposited directly on metallic surfaces other than copper. Also, the hydrogen evolution at the cathodic surface in the strike solution provides an additional safety factor in cleaning, and decreases the excessive contamination of the main plating electrolyte.

The recommended temperature range of 68° to 80°C for the high efficiency cyanide copper electrolytes permits operation at current densities of 10 to 40 amp./sq ft at high electrode efficiencies (99%+). The brightest plate is obtained at 68° to 70°C, but the maximum cathode current is limited. Operation at temperatures in excess of about 80°C reduces the brightness but increases the maximum cathode current density limit.

Agitation is an important factor in realizing maximum speed of plating from the processes. The cathode current density, using cathode rod agitation rates of 2 to 5 ft/min, is limited to 15 to 20 amp./sq ft. Operation at higher current densities will give dull and "burned" deposits of inferior quality. Higher cathode-rod agitation rates and solution circulation are used to extend the useful operating range to as high as 60 to 75 amp./sq ft in certain cases. Solution agitation has found wide application, particularly in the large conveyorized units.

The plating characteristics of high efficiency electrolytes also can be improved by utilizing current manipulation⁸ techniques. In usual practice the polarity of the plating current is reversed at periodic intervals by reversing the polarity of the field current of the generator, or by means of a reversing contactor. The direct (plating) cycles disclosed by Jernstedt⁹ may vary from 2 to 40 sec, and the reverse (de-

plating) cycles may vary from $\frac{1}{2}$ to 10 sec. Copper coatings of superior quality can be made at greater speeds by current reversal operation than by conventional methods. Direct-current operation of the electrolytes at high current densities may give "burned" deposits of a dull and granular appearance after plating for periods of 10 to 30 sec. Momentary polarity reversal of the current removes the "burned" or inferior metal and leaves a dense and smooth surface for further deposition. The net current efficiency is lower because current is used in deplating metal from the parts. However, when higher current densities are used, a net overall increase in plating speed results.

The throwing power of the high efficiency electrolytes is improved by current reversal. Deposits of almost uniform distribution may be obtained over articles having irregular shapes. This prevents excessive buildup of metal on high current density areas and may yield significant savings in quantity of anodes consumed. Deposits made by using current reversal show a laminar type of structure. Significant improvement in surface smoothness results when this technique is used in depositing copper over a roughly polished surface. Current reversal copper plate is more ductile than that applied with direct current.

The current reversal technique, as used with the high efficiency cyanide copper electrolytes, is a recent development. The high efficiency cyanide copper electrolytes are basically ideal for use with current reversal. The observation that thiocyanate² functions as an anodic as well as a cathodic brightener may account, in part, for the unusual results obtained from current reversal.

A NODES

Cast or rolled copper anodes are not recommended, since they tend to form heavy sludges during electrolysis. These sludges reduce the current densities at which the anodes may be operated, and contribute appreciably to roughness on upper horizontal surfaces of the cathodes. Electrolytic sheet copper is recommended for anodes, because it introduces no objectionable impurities into the bath and may be operated at high current densities with minimum formation of polarization films.

SOLUTION FILTRATION AND DIAPHRAGMS³

An adequate filtration system is recommended in operating high efficiency cyanide copper plating electrolytes, especially for the plating of heavy deposits in the range of 0.00075 to 0.002 in. The filter units should be constructed of steel- or rubber-covered steel to avoid con-

tamination with non-ferrous metals such as lead, brass, bronze, and others which are soluble in the electrolytes. Filter aids of the cellulose and silicate types are used. High filtration rates, equivalent to a complete solution turnover in 10 to 15 min, are recommended for solutions which are not equipped with anode and cathode compartments separated by a cloth diaphragm.

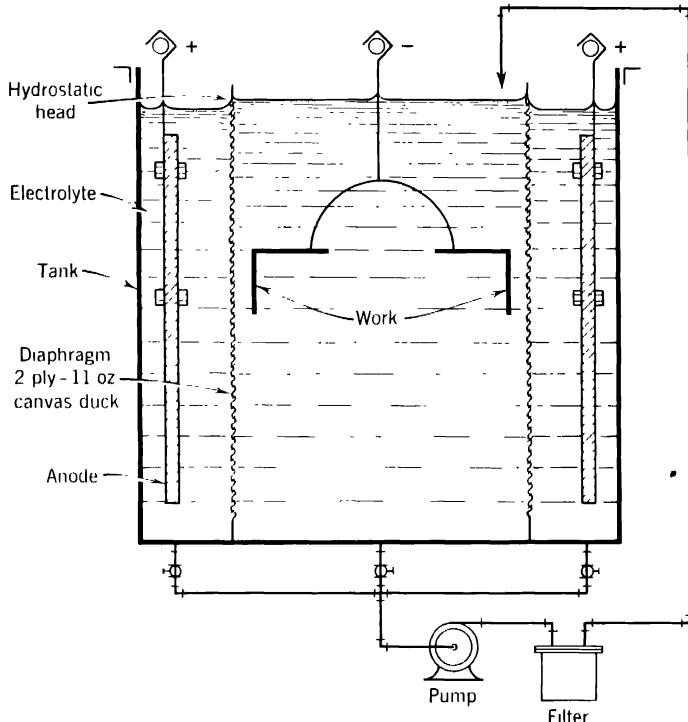


Fig. 1. Diaphragm installation.

Particle roughness has been encountered in commercial operation of high efficiency copper plating processes. Drag-in of foreign particles due to faulty cleaning, and the actual formation of metallic copper particles at the anode, are the main causes of this difficulty. The particles introduced by drag-in on the work may be eliminated by improved cleaning, and the roughness caused by particles formed at the anodes may be prevented by the installation of a semi-permeable canvas duck diaphragm as shown in Fig. 1.

A diaphragm-equipped tank is operated by pumping the solution from the anode compartment through a filter into the cathode compartment at a sufficiently high rate to develop a slight hydrostatic

head. The pressure formed by the hydrostatic head causes a solution flow from the cathode to the anode compartment and prevents migration of anode particles into the plating area. The pump and filter system, in addition to its function in maintaining a positive-directional head from cathode to anode, also insures that the electrolyte in each compartment does not get out of chemical balance as a result of electrolysis. For normal operating values this is equivalent to a total solution turnover of once in 4 to 6 hr.

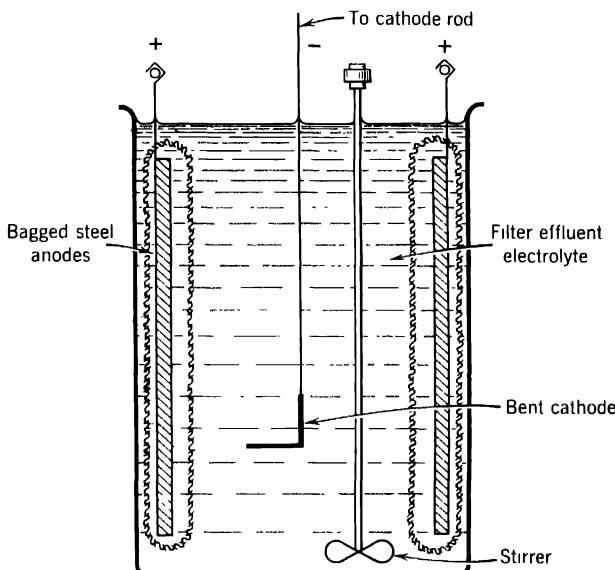


Fig. 2. Roughness test for filter effluent. Sample to be taken immediately before test. Test plate should be 0.002 in minimum.

Catholyte filtration rates, equivalent to a complete solution turnover once in every 2 to 5 hr, have been found suitable in most installations; this removes insoluble material carried in on the work or from the air. A separate pump and filter may be used for the cathode compartment, or a bleeder line from the cathode compartment to the low pressure side of the main pump may be installed as shown in Fig. 1.

Complete removal of particles from the solution filtered in transit from the anode to the cathode compartment is required for successful operation of the diaphragm system. Filtration efficiency may be tested as shown in Fig. 2. A sample of the effluent from the filter is transferred to a gallon beaker, and, without delay, a plating test is made on a bent cathode. A deposit of at least 0.002 in. should be made

at normal current densities, bagged insoluble anodes (steel is satisfactory) and vigorous solution agitation being used. Any roughness on the bent cathode shows unsatisfactory filtration.

Copper strike solutions may show a tendency to produce roughness, and, in such cases, a diaphragm should be installed in the strike tank. The same plating test as used for testing the efficiency of the filter (Fig. 2) can be applied to the strike solution. The bent cathode is cleaned and given a copper strike. Half of the upper horizontal surface is then wiped with a clean wet cloth and subsequently plated as described above. If the wiped area is smooth and the unwiped area rough, the roughness can be attributed to the strike.

The simplest form of diaphragm assembly is the Catholyte In-
closure. The diaphragm is constructed in the form of a rectangular
bag sufficiently large to enclose most of the electrolyte up to the
anodes. Braces may be installed on the anode side to maintain the
shape of the diaphragm, since the pressure will bulge the cloth toward
the anodes. The disadvantage of this type of design is the possibility
of damage to the diaphragm due to parts falling from the racks. An-
other adaptation of the diaphragm principle includes suspending the
anodes in metal frames enclosed in canvas bags. Solution from each
anode compartment is pumped through the filter into the cathode
compartment.

PURIFICATION

High efficiency cyanide copper electrolytes also require reasonable freedom from soluble impurities for optimum performance. Methods

TABLE 5. METHODS OF PURIFICATION

Identity	Source	
Dust, dirt, scale, etc.	Air, poor cleaning, poor housekeeping	Decantation, filtration, dia- phragms
Organic mate- rials, soaps, oils, etc.	Poor cleaning and rinsing, tank linings, rack coatings	Precipitated $Mg(OH)_2$ or acti- vated carbon ⁹
Zinc, lead	Die castings, lead and pew- ter castings	Electrolysis or precipitation with Na_2S
Chromium	Drag-in on racks from chro- mium tank	Precipitation with sodium hydrosulfite ¹⁰
Carbonate	Carbon dioxide from the air hydrolysis of $NaCN$	Freezing or precipitation with $Ca(OH)_2$ or $Ba(OH)_2$
Ferrocyanide	Drag-in from pickling tank	Freezing or precipitation with $Ca(OH)_2$ or $Ba(OH)_2$

⁹ Most of these purification treatments require filtration.

of purification will vary with the type of contamination. Table 5 indicates the general methods employed.

COMMERCIAL PLATING

The type of equipment used in plating from high efficiency cyanide copper electrolytes is dictated by the type of parts to be plated and the type of deposit required. Most still plating installations are small units, wherein the quantity of plating conducted does not justify the cost of conveyorized equipment. The parts are mounted on racks which are transferred manually through the cleaning, copper plating, rinsing, and subsequent plating operations. Plating time is determined by the current density and thickness required.

In semi-automatic operations the racked parts are handled manually through the cleaning operation, but the plating tank is provided with a conveyor which is loaded and unloaded at one position. The thickness of coating obtained is determined by the current density and the speed of travel of the conveyor, both of which can be varied as required.

The cleaning, plating, rinsing, and drying of the parts are conveyorized in the fully automatic type of operation. Time cycles in each tank are determined by the speed of the conveyor and the length of each tank. Current density, solution agitation, and bath temperature are adjusted to give the desired thickness and appearance of deposit. The plating time cycle is usually about 30 min for heavy deposits.

A typical plating cycle in a fully automatic unit for copper plating polished-steel parts such as bumper guards, grills, and other automotive trim parts, which are to be subsequently buffed, is shown below. Zinc die castings are treated in a similar manner, but the alkaline cleaning and acid dip operations are less drastic in action and are usually of shorter duration.

1. *Precleaning.* Solvent degreasers, immersion alkaline cleaners, or spray washers are used to loosen and remove the bulk of the oils and polishing compounds left on the work.

2. *Electrolytic Cleaning.* Parts are cleaned electrolytically in a heavy duty anodic-type alkaline cleaner. This treatment should complete the removal of oil, grease, polishing compounds, and other surface contaminants.

3. *Water Rinse (dip tank).*

4. *Water Rinse (combination dip and spray).* This rinse insures substantially complete removal of all cleaning solution from the surface before the parts are given an acid dip treatment.

5. *Acid Dip* (hydrochloric or sulfuric). This dip neutralizes any alkaline film on parts which have not been adequately rinsed, and also removes oxide films.

6. *Water Rinse* (combination dip and spray). Rinse should remove all acid from Step 5 before parts enter cyanide copper strike.

7. *Copper Strike*. This solution improves adherence of subsequent deposits and minimizes drag-in of contaminants into the high efficiency copper plating bath. Strike solutions commonly used contain 2 to 3 oz/gal CuCN, 0.75 to 1.5 oz/gal "free" sodium cyanide, 2 to 6 oz/gal sodium carbonate, and are operated at 49° to 66°C at 4 to 6 v. Parts are normally given a 30-sec to 3-min strike.

8. *Copper Plate*.

9. *Drag-Out Recovery Rinse*. This operation is recommended for recovery of electrolyte, which is then filtered and returned to the main plating tank for makeup or maintenance.

10. *Warm Water Rinse*.

11. *Warm Water Rinse*. Steps 10 and 11 should complete removal of all alkaline salts from the parts.

Barrel plating equipment may be divided into two types: individual barrel plating units and fully automatic types. The parts are usually cleaned in separate steel tumbling barrels, or in steel baskets in the individual barrel units. The parts are then transferred to individual plating barrels. After the parts are plated, the plating barrels are rinsed and the parts are removed for further rinsing and drying operations. Electrically operated hoists are usually employed to transfer the barrels from one tank to another. In fully automatic equipment all operations, including cleaning, rinsing, plating, are performed mechanically.

TESTING OF DEPOSITS

Most copper deposits used in decorative plating applications are plated with subsequent coatings of nickel and chromium. The thickness of composite copper-nickel-chromium plates is usually measured by examining a suitably prepared cross section of the electrodeposit under a microscope.¹¹ The Aminco-Bremner Magne-Gage¹² may also be used for measuring thickness of copper deposits on steel. This is a "non-destructive" test and is used extensively. The "drop testing" method developed by Hull and Strauss¹³ can also be used for determining thickness of copper deposits. A solution containing ferric

chloride (60 oz/gal), antimony oxide (2.7 oz/gal), and glacial acetic acid (250 ml/l) is used in this test. This method is reported to be accurate to within $\pm 10\%$.

PYROPHOSPHATE COPPER

J. E. STARECK *

The pyrophosphate copper plating solution † introduced in 1941 is used in the copper plating of zinc, aluminum, and steel parts. It is also employed for such special applications as a stop-off for nitriding^{1,‡} and selective carburizing,^{2,§} a drawing lubricant for stainless steel and

* United Chromium, Inc., Detroit, Mich.

† Sold commercially as Unichrome alkaline copper.

‡ References for this portion of the chapter will be found on pages 230 and 231.

steel,³ and for the prevention of hydrogen embrittlement.⁴ Much recent interest is also shown in its favorable waste disposal properties.

The use of pyrophosphates in the electroplating field is not new, and references in the literature go back more than a hundred years. Early progress, however, was slow, partly because of the poor state of development of the art at that time and partly because of the unavailability of proper commercial chemicals.

Roseleur⁵ used a pyrophosphate gilding solution as early as 1847 and soon thereafter also recommended a pyrophosphate bath for tin plating. Gutensohn⁶ obtained, in 1883, a patent describing a pyrophosphate type of electrolyte for the copper plating of lead, zinc, aluminum, and nickel articles. Since that time the names of Brand,⁷ Delval,⁸ Royer,⁹ and Regelsberger¹⁰ are the principal ones associated with the state of the art up to about 1912. Except for a review of the earlier references,¹¹ little further work seems to have been done in the field until the early thirties. At that time Stareek¹² began studying the pyrophosphate copper system first as a component of the electrolytic color plating solution. The strong tendency, however, of such baths to deposit copper metal rather than cuprous oxide eventually led to the separate development of the alkaline pyrophosphate copper plating process which is in commercial use today. The principal features of this process were described in 1941 by Coyle.¹³ Since that time a number of patents¹⁴⁻¹⁶ have been issued on the subject and several review articles¹⁷⁻¹⁹ have appeared in the literature.

PRINCIPLES

The bath most widely used today contains potassium copper pyrophosphate as an alkaline complex compound in aqueous solution. Potassium pyrophosphate reacts with copper pyrophosphate to form the highly soluble complex compound, $K_6Cu(P_2O_7)_2$, which may be isolated from the solution as the hexahydrate. The corresponding sodium salt,²⁰ $Na_6Cu(P_2O_7)_2 \cdot 16H_2O$, is more highly hydrated. In either case the copper is present as the complex anion, $Cu(P_2O_7)_2^-$.

Because of the greater solubility of the potassium compound and the higher transference number of potassium ion, the potassium type of bath is generally used in preference to the sodium type. The superiority of potassium, however, is not unique with pyrophosphate complexes, and today potassium salts are common in other plating solutions of alkaline complexes, as, for example, cyanides, lactates, and stannate.

BATH COMPOSITION

Besides copper and pyrophosphate, the bath in general use also contains ammonia, oxalate, and nitrate as auxiliary constituents. The concentrations of the various bath ingredients may be varied widely to give satisfactory plating baths.

The optimum concentration range for each constituent is given in Table 1.

TABLE 1. OPTIMUM RANGE OF BATH COMPONENTS

Analytical Constituent	Grams per Liter	Ounces per Gallon
Copper	22-38	3-5
Pyrophosphate	150-250	20-33½
Oxalate	15-30	2-4
Nitrate	5-10	2½-1⅓
Ammonia	1-3	1½-3⅔

The function of the pyrophosphate, as already indicated, is to form a highly soluble complex compound with copper. Some excess pyrophosphate is desirable to increase the conductivity of the electrolyte and to effect proper corrosion of the anodes. The ammonia also assists anode corrosion and adds somewhat to the luster of the deposit. The oxalate aids anode corrosion and helps stabilize the pH of the bath in operation. It also adds to the luster and general appearance of the deposit. The main function of the nitrate radical is to increase the operating current density by inhibiting the reduction of hydrogen at the upper end of the current density range.

OPERATING CONDITIONS

The pyrophosphate copper plating bath may be operated over a wide range of concentrations, temperatures, and current densities. The operating conditions most commonly used are outlined in Table 2.

TABLE 2. OPTIMUM OPERATING CONDITIONS

pH	8.2-8.8
Ratio P ₂ O ₇ /Cu	7.0-8.0
Temperature	50-60°C (122-140°F)
Voltage	1.5-4
Current density	10-75 amp/sq ft
Current efficiency	100% (approx.)
Anode to cathode ratio	1/1 to 2/1
Air agitation (vol/sq ft of surface)	1 to 1½ cu ft/min

The *pH* of the solution is maintained between 8.2 and 8.8 in accordance with measurements by a *pH* meter or *pH* papers. If the *pH* is too high, anode corrosion falls off. If the *pH* is too low, the throwing power of the solution and the stability of the complex decrease.

Operating current densities up to 75 amp/sq ft and higher may be used. The operating temperature is usually between 122° and 140°F.

The efficiency at both the cathode and the anode is approximately 100% under normal conditions of agitation and bath balance.

Continuous agitation of the solution is desirable. Air agitation is preferred because it provides good circulation of the solution and performance of the anodes as well as of the cathode. It is simple and convenient, and is permissible because it produces no buildup of carbonates in the bath. Mechanical agitation is also satisfactory. Agitation of the solution increases the operating current density range, as does increasing temperature.

MAINTENANCE AND CONTROL

FILTRATION

Either continuous or occasional batch filtration is recommended to remove dirt and insoluble matter which may otherwise give rise to rough deposits. Occasional carbon treatment is used to remove oils and buffering compound contaminants. When carbon is employed, it must be completely removed from the solution by filtration to avoid rough deposits.

PURIFICATION

The pyrophosphate copper solution is not sensitive to most of the impurities commonly encountered in plating operations. However, lead, cyanide, and oil are detrimental and tend to cause streaky and dull deposits and adversely affect the current density range.

Lead contamination is prevented by avoiding lead coils, linings, filters, or fittings. It may be removed by electrolysis. Cyanide contamination may be corrected by treatment with hydrogen peroxide. Oil is removed by filtration with activated carbon.

ANALYTICAL METHODS

In the control of the Unichrome alkaline copper plating solution, analyses are made for copper, pyrophosphate, and ammonia. The nitrate and oxalate in practice are automatically regulated by propor-

tionate additions with the pyrophosphate maintenance materials. The following methods of analysis are used.

DETERMINATION OF COPPER

1. Pipette a 5-ml sample into a 250-ml Erlenmeyer flask.
2. Add 10 ml of 1:1 sulfuric acid solution and cautiously take to SO_3 fumes on the hotplate. Cool and dilute to 100 ml with distilled water. Heat 3 to 5 min and cool.
3. Add 10 ml of potassium iodide solution (400 g/l potassium iodide).
4. Run in standard 0.1 N sodium thiosulfate solution ($\text{Na}_2\text{S}_2\text{O}_3$) from a burette until the color changes from a brown to a light yellow.
5. Add 3 ml of starch indicator solution.
6. Continue the titration until the blue color just disappears.
7. Calculate the ounces per gallon copper (Cu) present according to the following equation:

$$(\text{ml } \text{Na}_2\text{S}_2\text{O}_3)(N \text{ Na}_2\text{S}_2\text{O}_3)1.7 = \text{oz/gal Cu}$$

DETERMINATION OF PYROPHOSPHATE

The pyrophosphate content may be determined by the color indicator method, in which the endpoint is indicated by the change in color, or by the electrometric method, in which the endpoint is indicated by the pH reading, a glass electrode being used. The preparation of the sample is the same for either method.

Preparation of Sample. The copper content is removed by treatment with hydrazine sulfate and filtration with activated carbon.

Electrometric Titration.

1. Pipette 50 ml of the filtrate from the sample into a 400-ml beaker, dilute to 100 ml, add 3 to 4 drops of 1.0% phenolphthalein, and add concentrated hydrochloric acid a drop at a time until the red color changes to a light pink or becomes colorless.
2. Immediately titrate with approximately 0.5 N sulfuric acid to a pH of 3.8, stirring rapidly.
3. Add 50 ml of a 125 g/l solution of zinc sulfate and allow to stand for 4 to 5 min, with occasional swirling.
4. Slowly titrate back to a pH of 3.8 with continuous stirring, using standard 0.3 N sodium hydroxide, and record the volume of sodium hydroxide used.
5. Calculate the ounces per gallon of pyrophosphate ($\text{P}_2\text{O}_7^{-4}$) present according to the following equation:

$$\text{ml NaOH (pyrophosphate factor for NaOH)} = \text{oz/gal } \text{P}_2\text{O}_7^{-4}$$

Determination of Ammonia. Ammonia is simply determined by the well-known Kjeldahl distillation method. The ammonia gas is absorbed in excess standard acid, and then back titrated with standard sodium hydroxide to a methyl red endpoint.

ANODES

Electrolytic copper sheet or rolled electrolytic copper anodes are preferred, though cast anodes of good grade and purity have also been used satisfactorily. The anodes should be free of tin, nickel, silver, and lead, as these metal impurities tend to promote roughness of the deposit. Normally the anodes corrode evenly and bags are not used, as they interfere with the best solubility of the anode by decreasing the circulation of the solution at the anode surface. The anode current density can be fully as high as the cathode current density without encountering passivity.

PREPARATION OF BASIS METAL

The conventional cleaning cycles in general use are satisfactory for pyrophosphate copper plating, except that for steel and zinc die cast a preliminary strike deposit is applied. The strike solution may be a dilute cyanide copper, dilute pyrophosphate copper, nickel, or other type. If a cyanide copper strike is used, adequate rinsing or preferably a mild acid dip following the strike is recommended prior to final copper plating in the pyrophosphate bath. No special activating treatment after copper plating is required before bright nickel is applied.

TESTS OF DEPOSIT

Specifications for the thickness of plate and methods of testing are the same as those commonly used for other copper deposits. A series of standard specifications using copper in combination with other metals has been adopted by the American Society for Testing Materials²¹ for use by industry.

ACID COPPER ELECTROPLATING AND ELECTROFORMING

WILLIAM H. SAFRANEK * AND J. HOMER WINKLER *

Electrodeposition of copper from acid baths is extensively used for electroforming, electrorefining, manufacture of copper powder, and, to a lesser extent, for electroplating. Refiners and electroformers, in particular, employ acid solutions because costs of chemicals and current are low and because the baths are simple and easy to control. Electroformed copper articles (of manufacture) are produced by several important fields of industry, including electrotypes, sound records, band instruments, heat exchangers, and reflectors. More than 2500 tons of copper anodes are consumed in making electrotypes, valued at more than \$72,000,000 annually (1950). Modern methods of electrotype molding differ greatly from the procedures of the early forties. Recent developments have been announced concerning the electroforming of

* Battelle Memorial Institute, Columbus, Ohio.

complex shapes with re-entrant angles, which cannot be made by other methods, for radar, aircraft, and other industries.

Electroplating uses of acid copper baths include the building up of copper undercoats for nickel plate on steel or zinc die-cast parts that are initially given a "strike" plate in a cyanide bath. Many thousands of such parts are produced yearly and are assembled into articles

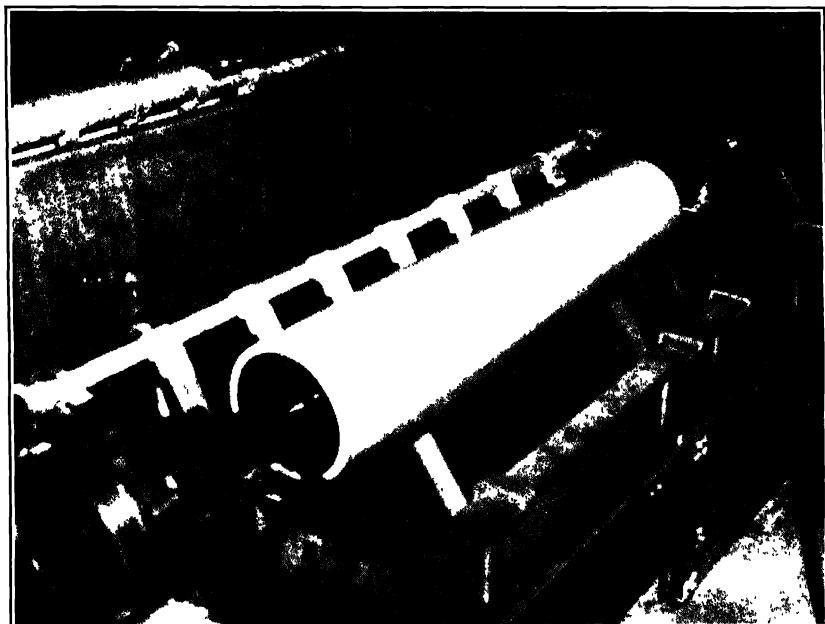


Fig. 1 The electrodeposition of copper on the outer surface of a steel cylinder for gravure printing. Cylinder is being rotated during plating operation. An average thickness of 0.008 in. is deposited for this purpose. (Courtesy of Art Gravure Corporation of Ohio, Cleveland, Ohio.)

intended for military, industrial, residential, and office application. The extent to which acid baths are used for this purpose has varied from year to year, depending on the relative costs of chemicals for acid and for alkaline baths and labor costs for buffing. Recent developments in bright plating may soon promote an increased utilization of acid solutions for depositing copper undercoats for bright nickel.

Miles of steel wire are given a copper cyanide "strike" and plated with copper in acid solutions to produce a high strength electrical cable. Thick deposits of copper (0.008 in.) are applied to steel rolls and then engraved for use in printing and marking paper and textiles (see Fig. 1). Plastics are coated with silver and then plated directly with

copper from acid baths. Stainless steel cooking vessels are copper plated in acid baths to improve the heat diffusion characteristics of outer surfaces. Copper plating for "stopping-off" carburizing on selective areas is accomplished by striking in a cyanide bath followed by plating in acid solutions. Building up of worn or overmachined parts is sometimes performed by acid copper deposition, especially when copper surfaces are desired for protection against fretting corrosion.

Metal powders, produced by deposition in acid baths, are used for making sintered compacts and pigments. In the electrowinning and electrorefining industries, acid baths are employed exclusively. More than 80% of the domestic production of primary copper is refined electrolytically.

HISTORY AND DEVELOPMENT

A literature reference to acid copper deposition was made as early as 1810.¹ It is said that Bessemer plated small castings in 1833.² The first patent disclosing a process for making electrotypes was granted to Jacobi in 1840.³ Since discussed commercial copper plating processes in 1843.¹ During the next seventy years progress was principally directed toward developing specific applications for acid copper electrodeposition. Publications during this period were reviewed by Bennett.⁵ Most of these references deal with copper sulfate-sulfuric acid baths, but oxalate,⁶ nitrate,⁷ acetate,⁷ fluosilicate,^{8,9} and cuprous chloride⁸ solutions are also mentioned.

Since World War I the literature has included much technical information and data on the copper sulfate bath. Winkler¹⁰ and Bandes¹¹ reviewed some of these papers. The procedures used before 1930 for depositing copper from the sulfate bath were described in detail by Blum and Hogaboom.¹² An early theory of the action of addition agents was discussed by Taft.¹³ Other acid baths investigated during this period were sulfate-oxalate-boric acid,¹⁴ sulfate-oxalate,^{15,16} cuprous chloride,¹⁷ cuprous chloride-sodium thiosulfate,¹⁸ benzene disulfonic acid,¹⁹ and cuprous iodide and bromide.²⁰

Since 1940 the most significant development in the deposition of copper from acid baths was the work on fluoroborate solutions,^{21,22} which, in less than five years, were advanced to a position of commercial acceptability. Until this time the copper sulfate bath was the only acid solution of commercial importance. The alkane-sulfonic acid bath was also invented during this period,²³ but it has not yet attained a position of commercial significance. Another solution, sulfamic acid,

was reported to produce acceptable copper deposits.²⁴ A solution of cupric formate and ammonium salts was operated at a pH of 2.0 to 4.0.²⁵

New applications as well as new methods have been developed in recent years. In the field of electroforming, especially, many new processes have been, or are, in process of commercial development. It is not possible to mention all literature references to acid copper deposition in this space, since the total number exceeds 1000. For example, more than 350 U. S. patents relating to electrotyping were granted before 1948.²⁶ Over 400 were issued from 1948 to 1953.

PRINCIPLES

The cupric (Cu^{+1}) salts in either the sulfate or the fluoborate bath are highly ionized except for small amounts of less ionized complex salts formed with certain addition agents. The addition of sulfuric acid to the sulfate solution, or fluoboric acid to the fluoborate bath is necessary for obtaining acceptable deposits. Because of the high conductivity of commercial solutions, and because anode and cathode polarizations are small, voltages required for depositing copper are less for acid than for alkaline baths. Electrorefining plants employ the copper sulfate bath largely for this reason. Tank voltages for refining copper are frequently as low as 0.2 v for a cathode and anode current density of 15 to 20 amp/sq ft.²⁷

Anode and cathode polarization are nearly negligible in purified solutions used at low current densities. Even at the high cathode current density of 200 amp/sq ft, a 6-v current source is ample when the solution is efficiently agitated. Excessive polarization of the anodes in the sulfate bath might occur if the anode current density exceeds about 47 amp/sq ft. With the fluoborate bath, the anode current density can be at least 375 amp/sq ft without encountering excessive anode polarization.

Because of the low cathode polarization potential, the acid baths do not have as good throwing power as alkaline solutions. The plate distribution closely approximates the primary current distribution; the deviation was found to be 10.8% or less for the sulfate bath.²⁸ This disadvantage is largely overcome in electroforming practice by appropriate current shields.

Anode and cathode efficiencies are nearly 100% at low and high current densities. The rate of deposition obtainable is chiefly dependent upon the efficiency of agitation in preventing excessive polarization. Acceptable deposits are reported to be secured at a current

density as high as 2400 amp/sq ft, equivalent to 3.63 mm/hr (0.143 in./hr),²⁰ with violent agitation.

The character of copper deposits is influenced by the concentration of copper salts, concentration of free acid, temperature, cathode current density, and the nature and degree of agitation. Dense deposits with good surface smoothness up to a thickness of 0.51 mm (0.020 in.) or more can be produced without addition agents. To brighten or harden the plate, one of several addition agents can be utilized.

FUNCTIONS OF BATH CONSTITUENTS

PRIMARY CONSTITUENTS

Copper sulfate and sulfuric acid, or copper fluoborate and fluoboric acid, are the primary constituents of the sulfate and fluoborate baths respectively. The cupric salts furnish the metal ions in solutions such as those given in Table 1. Copper is deposited at very low cathode current densities from the aqueous solutions of the salts,^{20, 31, 21} but at higher current densities the deposits from the sulfate bath are spongy and contain occluded salts. Plate characteristics are improved, solution conductivity is increased, and anode and cathode polarization is greatly reduced when free acid is added to either solution.^{22, 21} The acid also prevents the precipitation of basic salts.

The concentration of copper sulfate is not particularly critical, although the solution resistivity is greater when the concentration is increased,³³ and anode and cathode polarization are slightly reduced.³⁴ A concentration of less than 8 oz/gal copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) results in a decreased cathode efficiency.³⁵ When very high cathode current densities are used, a high concentration of copper sulfate, within the limits given in Table 1, is recommended. The solubility

TABLE 1. FORMULATIONS OF COMMERCIAL ACID BATHS FOR DEPOSITING COPPER

Copper Sulfate Solutions	"Average" Concentration	Concentration Limits
Copper sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	25.2 oz/gal (188 g/l)	20.1-33.5 oz/gal (150-250 g/l)
Sulfuric acid, H_2SO_4	9.9 oz/gal (74 g/l)	6-15 oz/gal (45-110 g/l)
Specific gravity, at 25°C (77°F)	1.165	1.115-1.21
Resistivity, at 21°C (70°F) ³⁶	4.2-4.3 ohm/cc	
Copper Fluoborate Solutions	Low Concentration	High Concentration
Copper fluoborate, $\text{Cu}(\text{BF}_4)_2$	29.6 oz/gal (224 g/l)	59.2 oz/gal (448 g/l)
Fluoboric acid, HBF_4	2 oz/gal (15 g/l)	4 oz/gal (30 g/l)
Boric acid, H_3BO_3	2 oz/gal (15 g/l)	4 oz/gal (30 g/l)
pH (colorimetric)	1.2-1.7	0.2-0.6
Specific gravity, at 27°C (80°F)	1.17-1.18	1.135-1.36
Resistivity, at 27°C (80°F) ²¹	7.3 ohm/cc	

of copper sulfate is decreased when the sulfuric acid concentration is increased.³²

Copper fluoborate is more soluble than copper sulfate. Metal ion concentration can be more than double in the fluoborate bath in comparison with a copper sulfate solution containing 6.7 to 10 oz/gal of sulfuric acid.

Changes in sulfuric acid concentration have more influence than changes in copper sulfate concentration on solution conductivity and anode and cathode polarization. For example, specific conductivity is nearly doubled when the concentration of sulfuric acid is raised from 6.7 to 13.4 oz/gal.³⁷ An additional increase in free acid concentration to 26.8 oz/gal, which is the level widely used in electrorefining, reduces the solution resistivity from between 4.2 and 4.3 to between 1.6 and 1.9 ohm/ce.³⁸ Cathode polarization decreases when a small amount of sulfuric acid is added to a solution of copper sulfate, but increases as the acid concentration is increased until a maximum is reached at about 6.7 oz/gal. Changes in the concentration of copper sulfate have little effect on grain size, but some grain refinement was detected as a result of increasing the sulfuric acid concentration.³⁹

If the acid concentration in the fluoborate bath is too low (if pH is more than 1.7), deposits are dull, dark, and brittle. Boric acid is added to stabilize the bath and prevent decomposition of copper fluoborate. The addition of boric acid slightly increases resistivity. In a bath with concentrations of more than 2 oz/gal fluoboric acid or 29.6 oz/gal copper fluoborate, an increase in the concentration of either the salt or acid results in a reduced resistivity.

ADDITION AGENTS

Addition agents for brightening, hardening, grain refining, surface smoothing, increasing the limiting current density, and reducing trees are frequently added to the acid copper sulfate bath, but the use of a particular addition must be evaluated for each application, because undesirable characteristics can then be avoided. For example, many of the addition agents that have been proposed result in plate embrittlement. Deposition potentials are generally higher when addition agents are added. Cathode polarization is greatly increased by adding gelatin (0.0268 oz/gal)^{39,40} or glue.^{34,41} Additions of gelatin or glue result in grain refinement, but this refinement is apparently chiefly undirectional, since the structure remains columnar but becomes more fibrous.³⁹ An excess of gelatin will introduce porosity or organic inclusions or both in the deposit.^{42,43,44} Vastly different plate

characteristics are produced in baths containing gelatin from different sources.³⁰

The effects of glycocol (glycine), one of the amino acid products formed by hydrolysis of gelatin, have been established as similar to the effects of gelatin. Surface smoothening and grain refinement result, but to a lesser extent than when gelatin is added.⁴⁴ Phenolsulfonic acid is widely utilized in the electrotyping industry. Deposits become harder and smoother after a bath has been electrolyzed or "dummied" for a short time after an addition of phenol or phenolsulfonic acid.⁴⁵ In comparison with the effects of gelatin or phenolsulfonic acid, dextrin apparently has little effect.^{46, 47} Other addition agents that have been investigated are: peptone,^{48, 47} pyrogallol,⁴⁷ starch,⁴⁷ urea,⁴⁶ dimethylaniline,⁴⁸ laetic acid,⁴⁸ gum arabic (calcium and magnesium arabate),^{41, 44} gum tragacanth,⁴⁴ hydroquinone,⁴⁶ quinone,⁴⁵ sulfosalicylic acid,* hydroxylamine,⁴⁸ benzoic acid,⁴⁸ tannin,⁴⁸ resorcinol,⁴⁸ triisopropanolamine,⁴⁹ and triethanolamine.⁵⁰

The smoothening and grain-refining tendencies of addition agents are sometimes associated with the formation of complex ions with copper or of colloids at or near the interface of the cathode. Gelatin or glycocol, for example, forms complex ions with copper⁵¹⁻⁵³ and also exists in colloidal form.⁵⁴ Particles of colloids arising from additions of selenium and arsenic oxides have been observed by ultramicroscopic examination to concentrate at the cathode.⁵⁵ With 0.14 to 0.42 mg/l selenium oxide and 0.0065 to 0.13 mg/l arsenous oxide, grain structure was refined, surfaces were smoothened, and the density was improved. However, the ability of a colloidal or ionic addition agent to improve the deposit cannot be conclusively predicted in advance on the basis of a general knowledge of its ionic or colloidal behavior in electrolytes. Thus, in a cupric nitrate bath, colloidal-type addition agents are effective as cathode polarizers, but do not always result in surface smoothening or grain refining.⁵⁶ Grain-refining agents have often been found to act as cathode polarizers, yet others acted as cathode depolarizers.⁵⁷

BRIGHT PLATES

Mirror bright plates are deposited when some addition agents are used with appropriate operating conditions. Thiourea (0.4 g/l) in combination with black strap molasses (0.8 g/l) results in bright plating when the sulfuric acid concentration is 1.34 oz/gal and the temperature is 21°C.⁵⁸⁻⁶⁰ This and similar baths were at one time used

* B. Blum (U. S. Bureau of Standards), private communication to the authors.

for plating bright, undercoat copper, preparatory to bright nickel plating. A combination of thiourea with naphthylamine disulfonic acid and cadmium or nickel was reported to produce bright plate.⁶¹ More recently, sulfonated acetyl thiourea or sulfonated aryl and alkyl substitution products of acetyl thiourea were developed for bright copper plating from acidic baths.⁶² Another process utilizes the sulfonation products of sulfurized aromatic compounds prepared by reacting toluene with sulfur chloride or thionyl chloride in the presence of anhydrous aluminum chloride and sulfuric acid.⁶³ This process produces ductile plates that are a good basis for plating bright nickel and chromium without an intermediate buffering operation.^{64, 65} Acetyl cyanamide is proposed as a brightener for either the sulfate or the fluoborate bath.⁶⁶

OPERATING CONDITIONS

In practice, temperatures may vary from 18° to 60°C; however, a temperature between 32° and 43°C is more common, since the temperature can be maintained economically with little or no heating or cooling. An increase in the temperature of a particular solution results in a higher conductivity and reduced anode and cathode polarization.^{31, 39} One investigator reported that decreasing the temperature from 35° to 15°C brought about a considerable grain refinement in plates deposited at 28 amp/sq ft.³⁹ However, the effect of changes in temperature on grain structure and surface smoothness is less significant than the effect of changes in cathode current density.

Current density and agitation must be balanced in order to obtain deposits having the desired characteristics and properties. For producing electrotypes, cathode current densities of 150 to 200 amp/sq ft are generally employed when using the sulfate bath agitated with air. Plating on fast-moving, endless wire can be accomplished at 450 amp/sq ft.⁶⁷ Still higher current densities are used when appropriate agitation conditions can be applied. Impinging of jets of electrolyte on the surface of the cathodes is said to permit a current density of 2000 amp/sq ft. When movement of the work is impractical or when air agitation fails to provide good mixing at all significant surfaces, the current density is usually kept at 40 to 50 amp/sq ft. It is claimed that higher current densities are practical with the fluoborate bath when agitation is the same as for the sulfate bath.^{21, 22} Acceptable deposits 0.001 in. thick were obtained without agitation at 350 amp/sq ft.

In either the sulfate or the fluoborate bath, an increase in current density results in increased cathode polarization (but not to the extent noted for many other solutions). Yet one investigator found that agitation had little effect on cathode polarization in the sulfate bath (relative to current densities up to 83.5 amp/sq ft).³⁹ Cathode films become more depleted in cupric ion and more concentrated in sulfate ion concentration when the current density is increased.⁴⁰ Clear evidence has been reported of grain refinement due to increasing the current density.⁴⁰ An increase in current density from 9.3 to 65 amp/sq ft reduced grain size to about one-third.⁴¹ Another investigator reported that high current densities resulted in grain refinement but promoted nodules and tree growth.³⁹

PHYSICAL PROPERTIES AND STRUCTURE OF DEPOSITS

Good strength, hardness, and ductility are wanted, especially for electroformed copper. The physical properties compiled from published data on copper deposited from acid baths are given in Table 2. Changes in copper sulfate or sulfuric acid concentration have little effect on hardness, strength, or ductility. It was reported that an increase in temperature or an increase in current density resulted in a significant reduction in tensile strength.²⁹ Thick plates produced in the "high concentration" fluoborate bath are similar in properties to most sulfate-copper deposits.

Copper deposits from acid baths are generally much less stressed than copper plates from cyanide solutions⁴² or iron and nickel deposits.^{43,44} Thus, dimensional changes or cracking of electroforms, encountered when using some types of plating baths, is never encountered with copper deposited in the sulfate or fluoborate solutions. Quantitative measurements reveal that stress in copper plated in the sulfate bath is only 1.0 kg/sq mm (1400 lb/sq in.), or less, depending on the nature of the basis metal.⁴⁵ Stress is said to be increased when gelatin, gum arabic, dextrose, or glycine is added to the bath.⁴⁶

Copper is deposited as face-centered cubic crystals that are randomly oriented,⁴⁷ unless deposited at less than 14 amp/sq ft, when the basis metal can exert an influence on the structure so that crystals in the basis metal and plate are oriented similarly.⁴⁸ Hardness has generally been associated with fine grains,^{57,60} yet hardness can be increased by introducing crystal orientation in the absence of grain refinement.

Without addition agents, the fluoborate bath, like the sulfate solution, normally produces deposits that are columnar. Grain continuity

TABLE 2. PHYSICAL PROPERTIES OF THICK COPPER DEPOSITS FROM ACID BATHS

Type of Bath	Hardness (Vickers or Equivalent *)	Tensile Strength kg/sq mm	Tensile Strength lb/sq in.	Elongation (% in 2 in. or 5.08 cm)
Copper sulfate-sulfuric acid ⁷⁰	80	25.4	36,000	22
Copper sulfate-sulfuric acid ⁷¹	81	25.5	36,150	22
plus molasses ⁷¹	81	23.2	33,000	21
plus thiourea and molasses ⁷¹	170	56.5	80,280	3
Copper sulfate-sulfuric acid ⁷²		28	39,800	34
Copper sulfate-sulfuric acid ⁷³		23.8 26.5	33,800-37,700	26-39
Copper sulfate-sulfuric acid ⁴⁶	13.69 (38-63 Brinell)			
Copper sulfate-sulfuric acid ⁷⁴	51-65 (16-61 Brinell)			
Copper sulfate-sulfuric acid ⁷⁵	47.62 (50-64 Rockwell 15T)			
Copper sulfate-sulfuric acid ⁷⁶		28.0 33.0	10,000-48,000	
plus trimpropanolamine ⁶⁰		45.63	65,000-90,000	8-12
annealed at 650°C (1202°F) ⁷⁶		18.2 26.0	26,000-37,000	
cold-rolled, electroclad sheet ⁷³		40	56,800	5
annealed deposit ⁷²		21	29,800	19.50
deposition on rotating cathode interrupted to burnish deposit ²⁹		21.5 47.6	35,000-68,000	
Copper fluoroborate-fluorobic acid (low concentration, 49°C or 120°F) ²¹	41-42 (44-45 Rockwell 15T)	12.0	17,100	7.3
plus molasses ²¹	62-71 (64-70 Rockwell 15T)	20.8	29,800	11.0
high concentration, 19°C (120°F) ²¹	55-61 (59-63 Rockwell 15T)	20.8	29,500	11.5
high concentration, 32°C (90°F)		26.5	37,600	18.5
plus molasses †		19.6	27,900	6.5

* Where conversions to Vickers scale from other scales were made on the basis of A.S.T.M. conversion data for copper and copper alloys, hardness data in parenthesis correspond to the data originally reported.

† C. Struyk, private communication to the authors.

from the basis metal into sulfate-copper deposits has been detected by many investigators.^{81,82} Thus the structure of the deposit is often influenced by that of the basis metal. Cleaned and unetched basis copper, unlike etched basis copper, does not influence the crystal structure of copper plate produced in a sulfate bath.⁸³

MAINTENANCE AND CONTROL

Bath compositions under normal conditions of operation require only occasional adjustment. If drag-out from the sulfate bath is abnormally low, copper concentration might gradually increase and necessitate occasional dilution. Concentration control can be simply

and easily accomplished by measuring the specific gravity and determining the acid concentration. Lead anodes to replace about one eighth of the copper anode area will tend to keep the copper and sulfuric acid concentration fairly uniform. It is necessary to determine the exact ratio by trial and error for a specific installation. In Table 3 specific gravity readings are converted to concentrations of

TABLE 3. TOTAL CONCENTRATIONS OF COPPER SULFATE PLUS SULFURIC ACID IN SOLUTIONS OF GIVEN SPECIFIC GRAVITY *

Sp. Gr., 25°/4°C	Copper Sulfate plus Sulfuric Acid		Sp. Gr., 25°/4°C	Copper Sulfate plus Sulfuric Acid	
	(oz/gal)	(g/l)		(oz/gal)	(g/l)
1.01	2.7	20	1.13	29.1	217
1.02	4.8	36	1.14	31.3	234
1.03	7.0	52	1.15	33.6	251
1.04	9.1	68	1.16	35.9	268
1.05	11.3	84	1.17	38.3	286
1.06	13.4	100	1.18	40.6	303
1.07	15.7	117	1.19	43.0	321
1.08	17.8	133	1.20	45.4	339
1.09	20.0	150	1.21	47.8	357
1.10	22.3	166	1.22	50.2	375
1.11	24.5	183	1.23	52.6	393
1.12	26.8	200			

* From *Principles of Electroplating and Electroforming*, by Blum and Hogaboam, McGraw-Hill, New York, 1949, 3rd ed., p. 433.

copper sulfate and sulfuric acid. Copper content of a fluoborate solution can be approximated by gravity measurements, and acid concentration is controlled by measuring pH, using prepared colorimetric pH papers. Analytical methods for determining copper and acid (sulfate or fluoborate) concentrations are given in a subsequent section.

The concentration of addition agents is usually controlled by empirical methods such as evaluating the appearance of deposits on special bent or sloping cathodes immersed in beaker samples of the plating solution. An analytical method based on a bromination reaction⁴⁵ was developed for determining the concentration of phenol or phenolsulfonic acid.

Filtration requirements are dependent upon the dirt load of the air and any dirt brought in by the work. Although it is possible to maintain acceptably smooth deposits with only occasional batch filtration, continuous filtration is usually preferred as a prevention of roughness of the deposit caused by dirt suspended in the bath. Silica-bearing filter aids should be avoided when the fluoborate solution is filtered; filter papers are satisfactory.

EFFECTS OF IMPURITIES

In general, acid copper baths are more tolerant of ionic impurities than many other plating solutions. Many metallic ions introduced regularly by carry-over with the work or by dissolution of the basis metal (e.g., iron, nickel, or zinc) can be expected to accumulate in the bath, because conditions are usually not satisfied for effecting codeposition of such metallic impurities with copper. Nickel and iron reduce the conductivity of the sulfate bath to the same degree resulting from an equivalent concentration increase in copper.⁸⁴ The deposition potentials of arsenic and antimony are apparently near that of copper in the sulfate bath, since codeposition was reported to occur.⁸⁵ Arsenic and antimony in concentrations of 10 to 80 g/l and 0.02 to 0.1 g/l, respectively, embrittled deposits and roughened surfaces. However, additions of gelatin or tannin were effective in inhibiting codeposition of these impurities and prevented roughness and embrittlement caused by them. Small concentrations of the alkali metal and alkaline-earth salts were found to smoothen copper deposits.⁸ Tin salts were also reported to smoothen deposits and were, at one time, purposefully added to the sulfate bath to effect smoothening.⁸ Lead is completely precipitated and silver is partly so as the sulfate. If silver is a contaminant, a small percentage will be codeposited with copper.

Nitrates are reduced to ammonia at the cathode in copper sulfate plating baths.¹² Grain size was found to be refined as a result of a small contamination with chloride ion (2.7 mg/l).⁸⁶ Soluble silicates introduced in a bath are precipitated on cathodes.⁸⁷

In the fluoborate bath, lead is the only metallic impurity known to interfere with the deposition of ductile plates. However, it can be precipitated by adding sulfuric acid. Besides lead, metals like silver, gold, arsenic, and antimony might be codeposited with copper, but the effects of such impurities are not known.

Organic impurities originating from decomposition of addition agents or leaching of elastomeric tank linings sometimes embrittle deposits, but can be removed by treating the solution with an appropriate activated carbon, followed by filtration. α -Naphthylamine was identified as an injurious contaminant leached from certain rubber tank linings.⁸⁸ As little as 10 mg/l of α -naphthylamine caused an irregular pattern of uneven thickness of copper plate. Treatment with activated carbon is desirable when a new bath is being prepared—especially the fluoborate bath, which may be contaminated with impurities

leached from rubber shipping drums. An instance has been reported of embrittlement traceable to impurities leached from wood tanks.¹⁷

ANALYTICAL METHODS

Copper concentration in either the fluoborate or the sulfate bath can be determined electrolytically, or by a volumetric procedure involving the reduction of cupric ion by potassium iodide and titration with sodium thiosulfate solution. Ammonium hydroxide is added in excess to 5 ml of bath sample diluted to 50 ml with water. Excess ammonia is removed by boiling the solution. Then 1 ml of glacial acetic acid is added and the solution is again brought to boiling. After the solution is cooled, approximately 10 ml of a 20% solution of potassium iodide is added. Then the solution is titrated with a 0.1 *N* solution of sodium thiosulfate (24.8 g/l $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$). When the solution is light straw yellow, 1 to 2 ml of 1% starch solution is added and the titration is continued to the disappearance of the blue color of free iodine. Each milliliter of 0.100 *N* sodium thiosulfate is equivalent to 0.00636 g copper, or, for a 5-ml sample, 1.27 g/l copper, 5.00 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, or 4.73 g/l $\text{Cu}(\text{BF}_4)_2$.

Sulfuric acid concentration may be determined by titrating a 10-ml sample of the plating bath with 1 *N* sodium hydroxide, using a few drops of a 0.1% solution of methyl orange to detect a color change from purple to light green. Each milliliter of 1.000 *N* sodium hydroxide is equivalent to 4.9 g/l of sulfuric acid.

Fluoboric acid concentration may be determined by diluting a 5-ml sample of plating bath to 50 ml and titrating with 0.25 *N* sodium hydroxide while stirring the solution with a mechanical glass stirrer. The appearance of the first permanent turbidity marks the endpoint. A blank should be run on a copper fluoborate solution containing no free fluoboric acid. Blank values will be approximately 7.0 ml for 224 g/l copper fluoborate, 7.7 ml for 336 g/l copper fluoborate, or 8.4 ml for 448 g/l copper fluoborate. After the value for the blank has been subtracted, each milliliter of 0.250 *N* sodium hydroxide is equivalent to 3.13 g/l free HBF_4 .

Methods for determining trace amounts of lead,⁸⁹ nickel,⁹⁰ chromium,⁹¹ and chloride⁹² have been reported.

ANODES

Rolled or cast bars or electrolytic copper sheets can be used as anodes for either the fluoborate or the sulfate bath. Copper with suit-

able purity can be obtained in any of these forms. Cast anodes are not employed to the same extent as rolled bars or electrolytic sheets because, if the castings are comprised of large grains or contain large amounts of oxides, large particles might break loose and roughen the deposit before complete dissolution takes place. Fine crystal structure, such as that produced by cold-rolled bars, is desirable.

In either the sulfate or the fluoborate bath, cast, rolled, or electrolytic anodes become coated with films of finely divided copper or copper oxide or both. Agitating the bath with air removes many, but not all, of the fine particles, causing some to be dissolved by the free acid. If the work is racked so that cathode "shelves" lie in a horizontal plane, particles will settle out on these areas and roughen the plate. In such cases the anode sludge can sometimes be reduced and the deposits made smoother by raising the bath temperature or increasing the acid concentration. In one series of tests, less copper was found in anode films formed in fluoborate baths than was found in sulfate bath films.²¹

Fine copper particles can be prevented from reaching the cathode by bagging anodes with a material woven with a plastic yarn comprised of vinyl chloride and vinyl acetate copolymer. To allow good mixing of the solution adjacent to the anodes, bags are made in the form of envelopes, enclosing several anodes placed edgewise to the cathode. Bags or diaphragms can also be made of felt, glass wool, asbestos, or porous alundum.

To avoid excessive anode polarization, the anode current density in an unagitated sulfate bath should be not more than 47 amp/sq ft. A slightly higher current density can be used if the solution adjacent to the anodes is vigorously agitated with air. The anode current density in an unagitated fluoborate bath can be as high as 375 amp/sq ft. With air agitation, the current density can be increased to 500 amp/sq ft.

Because the cathode efficiency is usually only 99.0 to 99.5% and the anode efficiency is more nearly 100%, the copper concentration in a sulfate bath gradually increases if drag-out does not compensate. When this occurs, lead can be substituted for copper anodes, in whole or in part, until the copper sulfate is reduced to the desired concentration. An instance is reported where a preference existed for continuously using insoluble, conforming anodes in order to improve deposit thickness distribution.⁹³ Copper concentration was replenished by circulating the solution through an auxiliary electrolytic tank connected in series with the electroforming tanks. The electrolytic corrosion tank was equipped with soluble copper anodes and scrap.

On each side of a rotating disk cathode were microporous rubber diaphragms, which inhibited the diffusion of copper ions into the catholyte and kept the cathode efficiency at a low level. The insoluble anodes in the electroforming tanks were made with silver-lead alloy (1% silver).

An insoluble anode reported to be used in copper electrowinning was made of an alloy of copper, silicon, iron, and lead.³⁵ Graphite is the only electrically conductive material known to be insoluble as an anode in the fluoborate bath. When used as an anode, graphite produces a sludge of finely divided carbon particles.

EQUIPMENT

Lead-lined tanks are satisfactory for containing sulfate baths, but steel tanks lined with a suitable rubber composition or synthetic plastic are preferable, since, otherwise, the metal lining might act as a bipolar electrode and rob current from significant areas of the work. Lead linings or other lead equipment are rapidly attacked by copper fluoborate solutions. Lining materials that are generally suitable for either the sulfate or the fluoborate bath are: natural hard rubber, natural soft rubber, polymerized ethylene, or plasticized vinyl chloride polymers. Air lines can be made of hard rubber or polymerized vinylidene chloride. Special grades of carbon pipe and tubing make efficient heat exchangers or cooling coils. However, lead is satisfactory in the sulfate bath and is less expensive. Rubber or rubber-lined filters are used for continuous filtration, but stainless steel is satisfactory for short periods.

TESTS OF DEPOSITS

Each application for deposits from acid baths involves distinctly different tests. Joint specifications of the American Society for Testing Materials and the American Electroplaters' Society specify that the thickness of copper on nickel- and chromium-plated zinc and zinc alloys shall be 0.0004 in., minimum, for type F.Z.; 0.0003 in., minimum, for type K.Z.; and 0.0002 in., minimum, for type Q.Z.³¹ The thickness of copper can be measured directly on magnified microsections. On steel, magnetic instruments can be used for measuring the thickness of copper deposits.

Copper-plated steel wire for electrical cable is tested for thickness and thickness uniformity, electrical conductivity, and tensile strength. Electroformed shapes are frequently given physical tests, in order to

control strength and ductility, by determining such properties as hardness, tensile strength, elongation in tension, and resistance to impact or denting.

PREPARATION OF BASIS METALS

Because loose, non-adherent, displacement films of copper are formed on steel and zinc if these basis metals are immersed in acid copper baths, a cyanide copper "strike" plate is required before plating in acid baths. If the basis metal is completely "covered," the "strike" plate can be as thin as 0.00005 in. After plating in the cyanide bath, the work should be thoroughly rinsed, dipped in a dilute solution of hydrochloric or sulfuric acid to neutralize any undissolved alkaline material, and rinsed again before plating in the acid bath.

Nickel or nickel alloys, when appropriately surface activated by reverse current "etching" in sulfuric acid or other method, can be plated directly in an acid copper bath. Contact should be made to the work before immersion. Stainless and chromium steels are plated in acid baths with adherent copper deposits by first "striking" in a solution concentrated in sulfuric acid but dilute in copper sulfate (32 oz/gal sulfuric acid and 15 oz/gal $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).⁹⁵

MOLD AND MANDRELS FOR ELECTROFORMING

Metallic and non-metallic materials are used as molds or mandrels for electroforming. Surface passivity characteristics make chromium alloy steel, aluminum, magnesium, tantalum, and chromium plating over other metals useful as metallic mandrels that require neither a surface treatment for providing conductivity nor a separating film for providing ready removal of the electroform. Chromium-plated steel mandrels are especially useful for electroforming mass-produced, hollow center objects concentric around one axis, which are removable by impact, such that the mandrel but not the completed electroform can pass through the center opening of a die. Surface-passive metallic mandrels can be used repeatedly without intermediate surfacing treatments, although a thin film of graphite is sometimes applied before each use to facilitate the final separation of the deposit from the mandrel. A mixture of graphite and wax has been utilized as a parting medium in the electroforming of tubing that was subsequently drawn into trombone slides.⁹³ Graphite in a thin suspension with kerosene is sometimes used.

Temporary mandrels are made and used only once and then are deformed or destroyed when deposition is completed. Low-melting alloys containing lead, tin, bismuth, cadmium, or mercury, or combinations of these elements, are melted out and recast. In electroforming pitot-static tubes, low-melting mandrels were employed.⁹⁶ Aluminum and zinc can be cast or machined into mandrels and subsequently chemically dissolved.

Non-metallic materials used for mandrels are asbestos, asphalt, cloth, gelatin, glass, paper pulp, plastics, plaster, pottery and other ceramics, rubber, wax, and wood. Each of these must be made surface conductive by one of the procedures discussed herein after molding is completed. Plaster, wood, and ceramics require, in addition, sealing to fill pores near the surface.

A plastic consisting of vinyl acetate and vinyl chloride copolymer has found wide acceptance in the electrotyping industry as a molding medium. Impressions of printing surfaces are made in the heated plastic sheet which is then cleaned, sensitized with a stannous chloride solution, and silvered by simultaneously spraying an ammoniacal silver nitrate solution and a solution of a reducing agent such as hydrazine sulfate, formaldehyde, or hydroxylamine hydrochloride.⁹⁷ Such molds largely replace the graphitized wax and lead molds used formerly (see Fig. 2). Copper is deposited on the silver (using a low current density for a few minutes) until the metal film is thick enough to carry a higher current. Then the current density is raised to about 200 amp/sq ft or more for another 40 to 70 min until a shell of 0.007 to 0.015 in. is deposited (see Fig. 3). Flexing the plastic mold releases the shell. Edges of the electrodeposited shell are trimmed, and the back is tinned in preparation for backing up with electrotype metal, a lead alloy containing 3% Sn and 3% Sb. Fidelity of reproduction of the final electrotype is good enough to duplicate photoengravings containing more than 17,000 dots/sq in. (264 dots/sq mm) in 133-screen halftone subjects.

Original, master sound records are cut in wax or lacquered aluminum disks and then metallized by cathode sputtering gold or copper, or by silvering; chemical reduction methods like that used in the electrotyping industry⁹⁸ are employed. After electroforming and separating the mother negative from the original master recording, a metal master is electroformed on the negative and subsequently used as a mold for electroforming the number of record stampers needed for the production of a given record. To facilitate the separation of record stampers from the metal master, the master is dipped in a



Fig. 2. Removal of electrotype shell from wax mold. (Courtesy of Pontiac Electrotype & Engraving Company, Chicago, Ill.)



Fig. 3. A modern electrotype plating tank installation. A semi-automatic unit is shown in the foreground. A cycle of 1 hr is used to deposit 0.010 in. of copper. (Courtesy of Partridge & Anderson Company, Chicago, Ill.)

solution of potassium dichromate (2 oz./gal) before electroforming is started.

Optically accurate metal reflectors are electroformed by using a silvered, precision-ground glass mold.²⁹ More than 200 lb (91 kg) of copper are deposited on the silvered surface of a glass negative 60 in. (152 cm) in diameter and detached from the negative by radiant heating. A metal negative is electroformed on the metal positive and, finally, metal reflectors are made on the copper negative.

In addition to those mentioned, many other kinds of molds, parting mediums, and methods for making surfaces conductive have been used.²⁶ Each application usually employs unique or different materials and procedures that have been proven by trials and tests.

9. Gold

LOUIS WEISBERG * AND A. KENNETH GRAHAM †

Applications of gold electrodeposits are dependent on the unusual properties of this noble metal. Resistance to tarnish, to oxidation at elevated temperatures, and to attack by most chemicals, combined with relative scarcity, high price, and pleasing appearance, have limited gold to specific uses. Laboratory apparatus such as analytical weights and calorimetric bombs are gold plated for protection against fumes and chemical attack. Electrical contacts are gold plated where resistance to high temperature, oxidation, and low contact resistance are important. The gold plating of pen points, jewelry, musical instruments and silver-plated hollow ware adds beauty, tarnish resistance, and value to the object. More recently, reflectors for industrial heating with infrared radiation have been electrodeposited with gold where tarnish resistance and high thermal reflectivity are important. Gold electroplate is used quite extensively to protect the interior basis metal surfaces of gold-filled and rolled gold plate watch cases from tarnish and to present an attractive, rich appearance on opening the case. Manufacturers of vanity cases use 24-karat electroplate chiefly as a decorative coating. Some manufacturers of automobiles are now using gold electroplate on name plates for some models.

Very little has been published on the technology of gold plating, probably because there has been but little fundamental change in the methods for many years. Favored bath compositions have remained the same, although today gold is more commonly added as the cyanide, rather than as the fulminate, in preparing the cyanide type of solution. In the larger installations of more recent times, analytical control of solutions, gold anodes for solution upkeep, accurate control of the weight of deposit through ampere-hour meters, and drag-out recovery are recognized means of effecting economies. The cost of

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gold has discouraged much independent research in plating. The incentive for such effort is also lacking because high current density rapid plating of gold is not required to produce the thin coatings commonly employed. There is little reason to expect much change in the immediate future.

The principal application of gold plating is in flashing or "coloring" jewelry. Where the required color cannot be obtained with 24-karat gold, alloy deposits are used. These alloys are seldom under 22 or 23 karat (92 to 96% gold), yet they are often spoken of as "14 k," "16 k," and so on. This nomenclature is based on the practice of making up solutions for gold coloring by dissolving 14- or 16-karat alloy anodes by the porous cup method.

This discussion makes no attempt to deal with gold alloy plating, which is a subject of considerable importance in itself, but touches on the topic briefly in connection with the effect of various metals present as impurities in the gold-plating solution.

The use of thick gold electrodeposits in jewelry is limited. In most applications of thick deposits, alloys rather than pure gold are deposited and these may be subjected to heat treatment to give them the desired properties.¹

PRINCIPLES

Typical compositions of gold cyanide baths are 1, 2, and 3 in Table 1. They consist of gold (aurous) cyanide dissolved in excess alkali cyanide. Bath 3 was used during World War II for relatively heavy deposits (0.0002 in. or 0.0005 cm in thickness). Phosphate baths are claimed to produce deposits of lower karat shades than baths made without phosphate. An old, partly exhausted bath is frequently used for applying the first or "shading" coating. This may or may not be brushed before the final coating is applied in a fresh bath with higher metal content. This last step is called "coloring."

Bath 4 was used for rapid deposition of heavy gold 0.0005 to 0.001 in. (0.00125 to 0.0025 cm) in thickness, according to one reliable informant.

When very heavy gold deposits are required, a thin coating may be applied from a cyanide bath, after which a gold chloride solution is used. Such a solution^{3,4} may contain 28 g/l (3.5 troy oz/gal) of gold as auric chloride with 35 g/l (4.7 oz/gal) of hydrochloric acid (sp. gr. 1.18). The rate of deposition from the cyanide bath is higher for a given current density than from the trivalent gold chloride bath, and the throwing power is superior.

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TABLE I. TYPICAL GOLD CYANIDE BATH COMPOSITIONS

	Bath							
	No. 1 *		No. 2 *		No. 3 †		No. 4 ‡	
	oz/gal	g/l	oz/gal	g/l	oz/gal	g/l	oz/gal	g/l
Metallic gold,‡ as fulminate or cyanide								
Cyanide, KCN	0.25	2.1	1.0	8.4	1.2	10		22
	2.0 §	15.0	1.4	11.0	1.6	12		
Phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$								
Carbonate,	0.5	4.0						
Na_2CO_3 or K_2CO_3		variable				variable		
Ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$								
								200

* Reference 5, p. 304.

† Private source.

‡ Recorded in the formulas as troy ounces per gallon. Theoretically, $\text{Au}(\text{CN})_2 = 88\%$ gold; $\text{NaAu}(\text{CN})_2 = 72.5\%$ gold; $\text{KAu}(\text{CN})_2 = 68\%$ gold.

§ If NaCN is used in place of KCN, the bath concentration is 1.5 oz/gal.

In practice, gold deposits of sufficient weight to stand buffing or burnishing^{5,6} are produced from these baths. It has been reported* that gold deposited from a solution having very low metal and free cyanide content, i.e., 1.0 g/l potassium gold cyanide (67%) and 1.2 g/l free potassium cyanide, is more readily buffed to a high luster and has better abrasion resistance than deposits of equal thickness plated from the more conventional cyanide solutions. Very rapid agitation is employed along with current density of about 3 to 4 amp/sq ft, temperature of 65° to 70°C, and insoluble anodes, preferably platinum.

FUNCTIONS OF CONSTITUENTS OF BATH

Metal and complex ions in the cyanide bath are commonly supplied by the alkali metal gold cyanide, $\text{KAu}(\text{CN})_2$ or $\text{NaAu}(\text{CN})_2$.⁷ When operating with soluble anodes, the free alkali cyanide maintains the metal content of the bath. The sodium and potassium ions are be-

* Private communication from H. Seman Payne, Wadsworth Watch Case Co.

lieved to be equivalent in effect. Only in more concentrated cyanide baths, as with silver or copper, where relatively heavy deposits of some degree of luster are required, and where higher current densities are usually involved, has some evidence of superiority of potassium ions been presented. Carbonates and phosphates both serve as buffers⁸ and improve the conductivity of the bath. Small additions of alkali formate and ammonium benzoate have been recommended⁹ by means of which successful deposition of gold directly upon steel or ferrous alloys is claimed.

The metal content of the cyanide bath in practice may vary from 1 to 5 g/l (0.12 to 0.6 troy oz/gal; 2.44 to 12.2 dwt/gal). The free cyanide (potassium cyanide) may vary from 2.25 to 11.3 g/l (0.3 to 1.5 oz/gal). Both the metal and free cyanide concentrations are controlled within narrow limits for uniform results. Carbonate is frequently omitted from new baths since it builds up during operation. Better practice is to add a small amount, up to 15 g/l (2 oz/gal), usually of carbonate or phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. Without these buffers the pH may vary widely.⁸

The metal ions of the chloride bath^{3, 5} are supplied by the complex auric chloride (HAuCl_4) resulting from the solution of gold trichloride in hydrochloric acid. Excess acid or soluble alkali chloride maintains the metal content of the bath from the soluble gold anode and also improves the conductivity.

The concentration of gold in the chloride bath may vary from 16 to 32 g/l (2 to 4 troy oz/gal; 39 to 78 dwt/gal). The concentration of hydrochloric acid (sp. gr. 1.18) may vary from 90 to 150 g/l (12 to 20 oz/gal). For uniform results, however, both the metal and free acid content should be closely controlled.

When a large volume of gold solution is employed, the optimum gold concentration is the minimum that will give satisfactory deposits. The investment cost is thus limited, and drag-out losses are reduced.

When it is desired to apply a coating of gold which is very uniform in thickness and color, and which will withstand moderate service, but with less expense than with the regular gold plating, the so-called "salt water process" is often used. In this process the gold solution is contained in a porous cup or pot which is placed in a copper vessel filled with a strong solution of sodium chloride, in which a sheet of zinc is suspended. A small quantity of ammonium chloride (NH_4Cl) is also added at times. The solution is usually heated to about 70°C, thus hastening deposition.

The method involves the use of a primary cell and battery, in which the current is furnished by the zinc dissolving in the nearly

saturated solution of sodium chloride. The object to be plated is connected by means of a copper wire or rod to the zinc serving as an anode and is then immersed in the gold solution. Under these conditions the current is furnished by the cell instead of from an external source as in ordinary plating.

A typical formula⁵ for the gold solution in the salt water process is as follows:

Gold (as fulminate)	1.2 g/l	3.0 dwt/ga
Sodium ferrocyanide, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$	15.0 g/l	2.0 oz/gal
Sodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	7.5 g/l	1.0 oz/gal
Sodium carbonate, Na_2CO_3	4.0 g/l	0.5 oz/gal
Sodium sulfite, Na_2SO_3	0.15 g/l	0.2 oz/gal

Either sodium or potassium ferrocyanide may be used, and the gold content is sometimes reduced to as little as 0.4 g/l (1 dwt/gal). The solution is usually boiled for about 30 min and filtered before using. Since little is known about the properties of the bath ingredients and the manner in which they function, no further reference to salt water gold plating will be made here.

OPERATING CONDITIONS AND CHARACTERISTICS

Cyanide baths are operated at current densities of 1 to 5 amp/sq ft, temperatures of 40° to 80°C and about 2 to 5 v. Temperatures of 50° to 70°C are more common. Higher temperatures and higher metal concentrations permit the use of higher current densities. The current efficiency may approach 100% under favorable conditions of low current density, high temperature, and relatively high metal concentration with moderate free cyanide. It is quite common, however, to vary these conditions in order to obtain the shade of the deposit desired. In such cases, the efficiency may be higher at the anode than at the cathode.

In general, the pH of the gold cyanide bath is not controlled. In the absence of buffers the pH may vary widely, and for uniform results it should be controlled.⁸ Caustic soda has been recommended for producing a light rose gold, and carbonate for a dark rose gold.¹⁰

The ferrocyanide bath (4) was successfully operated during World War II at 82°C, 20 amp/sq ft, and with agitation to deposit up to 0.001 in. (0.0025 cm) in thickness in 20 min.

A current density of 5 amp/sq ft at 2 to 3 v and 24°C is recommended⁹ for the chloride bath composition given above. Higher current densities may be used at higher temperatures, and the more

concentrated bath should be employed under these conditions.⁴ The character of the deposit obtained usually determines the optimum values of current density and temperature. The current efficiency of this bath is uniformly high, but the throwing power is not so good as that of the cyanide bath.

MAINTENANCE AND CONTROL

In the jewelry industry, bath volumes are small and chemical control is not universally employed. An old cyanide bath is sometimes used for the first or so-called "shading" deposit, and a new bath is used for the final deposit. When the old bath becomes contaminated with metal impurities or is low in gold, it is sent to the refiner.

Larger installations usually employ analytical control of both free cyanide and metal concentration. The free cyanide and carbonate determinations are similar to those described for the rochelle copper bath in Chapter 8.

Pope¹¹ recommends that the gold be determined by evaporating a 25-ml sample of bath to dryness in a crucible, then fusing with potassium bisulfate. After cooling, distilled water is added, and the precipitated gold is filtered off, washed, dried, ignited, and weighed.

The volumetric method¹² is more commonly used. A 25-ml sample is placed in a 250-ml beaker. Then 15 ml of concentrated hydrochloric acid solution is added (under a well-ventilated hood), and the solution evaporated to a syrup over a water bath. About 150 ml of distilled water, 25 ml of 20% potassium iodide solution, and 2 ml of 1% starch solution are then added. The sample is titrated with 0.01 *N* sodium thiosulfate solution until the color disappears. The excess is then back titrated with 0.01 *N* iodine solution until the blue color appears. The exact number of milliliters of thiosulfate required for the gold titration is equal to the total number minus the milliliters of thiosulfate equivalent to the volume of iodine solution used. (The $\text{Na}_2\text{S}_2\text{O}_3:\text{I}_2$ ratio is frequently checked.) This value multiplied by a factor (grams of gold per milliliter for the standard thiosulfate solution \times 40) gives the grams per liter of metallic gold in the bath.

A method of decomposing the cyanide simpler than either of the above is to heat 25 ml of the gold solution with 15 ml of concentrated sulfuric acid and 3 ml of nitric acid in a Kjeldahl flask until fumes of sulfur trioxide are given off. The mixture is cooled, 100 ml of water is added, and then the whole is boiled for at least 15 min to coagulate the precipitated gold and dissolve the anhydrous sulfates of any other

metals that may be present. The gold precipitate is filtered off and determined gravimetrically, or it may be dissolved with 10 ml of concentrated hydrochloric acid and 1 g of potassium chlorate and titrated as above, after boiling to destroy any excess chlorate and drive off any free chlorine in the solution.

Further details regarding analytical control of gold plating solutions are available in the literature.¹²

Maintenance of the metal content in gold plating solutions is assisted by recovery of solution carried out of the plating tank on the objects being plated. Recovery of drag-out is also important for economic reasons. The reclaimed material may be utilized to make up evaporation losses of the plating baths, or the metal value may be recovered by treating the reclaimed solutions and sending the residues to a gold refiner. The economies of reclaiming operations¹⁴ and a practical method of recovering gold from the reclaimed solutions have been discussed in recent literature.¹⁵

Cyanide gold plating solutions suffer a loss in current efficiency when excessive amounts of carbonate have accumulated in the solution. Carbonate removal is seldom practiced, for it is usually considered more economical to recover the gold and make up a new solution.

Soap and similar materials are definitely harmful and should be kept out of the gold plating solution by thoroughly rinsing the work before plating. When necessary, materials of this type may be removed from the plating solution by treatment with carbon, but this must be done with care to avoid considerable loss of gold in the carbon.

Metallic impurities introduced into gold plating solutions are usually objectionable because they affect the color of the deposit. For example, copper changes the color from yellow to pink or red, according to the amount present. Silver and cadmium produce a green color, whereas nickel and zinc turn the color white or "pale." Lead results in the formation of a black, loosely adherent smut, which, however, finds application in producing certain antique finishes. Iron has little effect, if any, on the deposit, although many platers never fail to add a considerable amount of "prussiate of potash" whenever they prepare a gold plating solution. Under some conditions the addition of ferrocyanide has been observed to produce a marked lowering of current efficiency.

The usual methods for purifying cyanide plating solutions are applicable to gold solutions but, since these often involve some loss of metal, exceptional care is required; otherwise the loss of gold may not justify purifying the solution as compared to recovering the gold and making a new solution.

It is not always easy to regulate the rate at which gold anodes dissolve so as to maintain the metal content of the solution at the desired concentration. Many gold plating solutions are therefore operated with insoluble anodes. Besides, insoluble anodes require a smaller investment and offer less temptation to dishonest workmen. The use of insoluble anodes requires that gold be added to the solution from time to time in the form of salts.

A convenient way of maintaining a reasonably uniform metal content is to have an ampere-hour meter in the circuit and make additions on the basis of ampere-hour readings. It is a simple matter to determine the amount of gold required per ampere-hour for the conditions under which the solution is operated. In order to get reproducible results, it is necessary, of course, that the current density and temperature as well as the free cyanide be kept reasonably uniform. This method of operation may be set up so as to take care not only of the metal plated out but also of the drag-out losses.

The ampere-hour meter may be provided with a movable contact arm which causes a bell to ring or a light to flash whenever an addition is required. It is also convenient sometimes to provide an integrating or totalizing mechanism in the ampere-hour meter to keep a record over a long period of time. If this method is properly set up and followed with reasonable care, a gold plating solution may be operated for long periods of time with no chemical analyses except for the control of free cyanide. The same method has been applied to gold alloy deposits, where it affords means of controlling color and composition of deposit. This method is preferred in many cases to the use of alloy gold anodes. The principal disadvantage of this method is the accumulation of alkali carbonate formed from the cyanide introduced with the gold.

ANODES

Hard carbon, stainless steel, Nichrome³ and platinum⁴ are used as insoluble anodes in the cyanide bath. Good results have been obtained with ordinary 18:8 stainless steel. Steel containing molybdenum has been less satisfactory. Soluble, high purity, rolled-gold anodes are frequently employed in the cyanide bath. In some cases both soluble and insoluble anodes have been utilized to control the metal content of cyanide baths. With proper control of free cyanide, temperature and soluble anode area, however, good uniform results may be attained with insoluble anodes at intervals only to lower the metal concentration.

It has been reported¹⁶ that a gold anode is covered with a protecting layer of insoluble sodium gold cyanide when electrolyzed in sodium cyanide, but that potassium gold cyanide is soluble and does not produce the passive state. The latter statement is not entirely correct, because it has also been reported that with a very low concentration of potassium cyanide passivity will set in, accompanied by gas evolution. Furthermore, if the cyanide concentration is increased above about 2%, films of brown or yellow coloration, due to polymerized cyanogen compounds, are produced on the anode and render it passive. On the basis of more complete studies of the anode behavior of copper in a cyanide electrolyte, one might infer that the behavior of gold is entirely analogous and that the successful use of soluble gold anodes depends upon the control of the anode current density, free cyanide, and temperature.

Gold anodes are passive in a solution of HAuCl_4 , and chlorine is liberated.¹⁷ The addition of hydrochloric acid or a soluble chloride, furnishing chloride ion, or an increase in temperature will remove the passive state. In the gold chloride plating bath, a gold anode may also become passive even in the presence of free chloride ions if the anode current density is too high.¹⁸ Under these conditions the anode polarizes in a manner exactly analogous to that reported for the more common metals in cyanide plating baths.

PREPARATION OF BASIS METAL

Copper, brass, nickel, and silver are readily gold plated. Steel is usually first plated with one of the above metals. Silver-plated hollow ware is scratch-brushed wet and then gold plated. If gold is to be deposited on a buffed surface, the basis metal involved must be given its usual cleaning treatment prior to gold plating. Solder marks are often covered by an undercoating of copper, brass, or nickel.

Most gold deposits are very thin, and under these conditions the color of the undercoat sometimes influences the color of the plated object. With a gold deposit 0.000001 in. (0.000025 mm) or more thick, this effect is eliminated; therefore, where such a relatively heavier coating is used, one is not so limited in the choice of undercoat.

Gold plating of stainless steel (18% Cr, 8% Ni, 2.5% Mo) pen points requires special treatment because of the passive character of the basis metal. Several patents^{19, 20} have been issued which cover these treatments, the most practical of which involves the following steps:

1. Electrocleaning, alkaline.
2. Electropickling, 10 to 50% hydrochloric acid.
3. Gold plating in a bath containing 2.7 g/l (0.33 troy oz/gal; 6.64 dwt/gal) of gold and about 19 g/l (2.5 oz/gal) of free sodium cyanide. It is also recommended that for best results the work be connected to the cathode rod before it is immersed in the bath.

A more recent patent⁹ covering a method for gold plating directly upon steel and ferrous alloys recommends the use of an alkaline cleaner, a 0.5- to 2-min dip in a mixture of concentrated fluosilicic acid (H_2SiF_6), 35% hydrofluoric acid and water (65.3 and 32% by volume, respectively) and a gold cyanide bath similar to 1 in Table 1, but containing 0.25 g/l (0.034 oz/gal) of ammonium benzoate and sodium formate instead of phosphate as shown.

A brass undercoating is sometimes specified because there is less contrast in color if the gold wears through in some places. Nowadays, the gold plate is usually protected by a covering of transparent lacquer (baked on) where the utmost in wear is required. All things considered, a nickel undercoat is the most satisfactory because of the intrinsic protection it affords. For example, costume jewelry made of brass or white metal plated first with about 0.0002 in. (0.005 mm) of bright nickel, then with only enough gold to give the desired color, and finally covered with a good grade of baked transparent lacquer has been found to stand up so well that failures in service are practically negligible.

The preparation of solid gold jewelry and of costume jewelry for gold plating is also described in two recent articles.^{21,22} The finishing of band instruments is given in some detail.²³

TESTS OF DEPOSITS

THICKNESS—SPECIFICATIONS

The thickness of gold applied is nearly always limited by considerations of cost. In most applications the quantity put on is usually the least that will give a satisfactory color. Gold plating is sometimes employed in the jewelry industry to apply thick deposits of specified intrinsic value, but in this case alloy gold deposits are generally preferred. In electronic applications during World War II deposits from 0.0002 to 0.001 in. (0.0005 to 0.0025 cm) are known to have been used.

The thickness of gold plating used in the jewelry industry may eventually be expected to conform with certain standards for marking which the industry is now engaged in setting up under the auspices of the National Bureau of Standards. These standards (TS-3131) are in only tentative form at present. Jewelry or other articles carrying not less than 10 parts per 1000 of fine gold by weight may be marked with the words "gold content" or "gold electroplate" followed by a decimal expressing the actual gold content, for example, 0.010 or 0.025, as the case may be. It has been proposed to limit the use of the words "gold plated" to deposits carrying a minimum thickness of 0.00018 mm (0.000007 in.) on significant surfaces, but up to the time of this writing the proposal has not been adopted.

The amount of gold on jewelry is usually determined by fire assay. In dealing with very thin coatings, fire assay methods cannot be relied on. It is necessary to strip the gold coating and determine the gold removed by a suitable method of analysis. It is important also to make sure that the sample used is representative of the whole lot, for there may be exceedingly large variations in the quantity of gold found on separate pieces. The results obtained by examining a few pieces or examining pieces improperly selected may be altogether misleading. The number of pieces taken should be large enough to give a weight of gold that can be accurately determined.

Stripping thin gold deposits is easily accomplished if a nickel under-coat is present, for then it is only necessary to make the pieces anodic in a cyanide solution for a short time. On copper or brass, the gold may be stripped anodically in a solution containing about 5% of hydrochloric acid. Another method that may be used is the combined action of sodium cyanide and hydrogen peroxide. In this method, hydrogen peroxide is added gradually to a 2% solution of sodium cyanide with which the pieces to be stripped have been covered. If the peroxide is added too fast, the solution heats up rapidly, and the reaction may get out of hand. Stripping in this solution is facilitated by bringing the pieces to be stripped in contact with a piece of platinum or nickel. It is sometimes difficult to tell when all the gold has been removed and to avoid dissolving considerable amounts of basis metal. In the case of gold over a brass undercoating on steel, both brass and gold should be stripped to insure that all the gold is stripped. Needless to say, any lacquer present must be removed with a suitable solvent before an attempt to strip the gold is made.

The gold present in the stripping solution may be determined either gravimetrically or volumetrically. If a cyanide stripping solution is

employed, the first step is to destroy the cyanide. This may be done by any of the methods described for analyzing cyanide gold plating solutions. Since the quantity of gold involved may be rather small, care must be taken that the method employed to determine the gold is sufficiently accurate for the purpose.

A convenient method for determining small amounts of gold, specifically for the purpose of ascertaining the thickness of electro-deposited gold coatings, has been published by Clabough.²⁴

ACCELERATED CORROSION TESTS

A test reported for gold deposited over nickel uses a reagent consisting of 3 g of agar and 6 g of sodium chloride dissolved in 100 cc of water. This solution is made slightly ammoniacal with ammonium hydroxide, and then 10 cc of a half-saturated alcoholic solution of dimethyl glyoxime is added. The coated article to be tested, connected to the positive pole of a 6-v storage battery, is placed in a small dish and covered with the warm reagent, which is then allowed to gel. A layer of saturated sodium chloride solution is poured over the gel and a platinum wire cathode immersed in the solution. A current density of 5 to 10 ma/sq cm is then employed, and small red spots appear in 5 to 10 sec at all points where nickel is exposed.*

The porosity of gold coatings on brass may be strikingly detected by the exposure of the gold-plated parts for several hours to a mixture of air and nitric acid vapor under a bell jar at room temperature. Discontinuity of the coatings is revealed by fine "whisker-like" protrusions of blue corrosion products which develop on the side of the pores.*

Gold deposits are often rated by the length of time they withstand the action of nitric acid. Although this test may be used to compare the relative thickness and porosity of different coatings, it has not been standardized, and, accordingly, when one says that a given gold deposit "withstands nitric acid for one minute," this is not sufficiently descriptive. A useful test for thin coatings is to subject them to the action of moist hydrogen sulfide for several hours. Any porous spots in the gold will appear black or brown through discoloration of the basis metal. For thicker gold deposits, the weight or thickness of gold may be determined satisfactorily either by fire assay or by wet methods.

* Test developed by C. H. Sample of the Bell Telephone Laboratories, New York, 1937.

THICKNESS

It has been reported that gold coatings may be deposited on brass in thicknesses of the order of 0.0001 in. (0.0025 mm) which show no evidence of pinhole corrosion in the usual accelerated corrosion tests. Generally for contact surfaces deposits of 0.0005 in. (0.0125 mm) are recommended.²⁵

TABLE II. UNITS

	Pounds avoir.	Pounds troy	Ounces avoir.	Ounces troy	Grams
lb (avoir.)	1.000	1.215	16.0	14.58	453.6
lb (troy)	0.823	1	13.17	12.0	373.2
oz (avoir.)	0.0625	0.076	1	0.911	28.35
oz (troy)	0.0686	0.0833	1.097	1	31.10
g (metric)	0.00221	0.00268	0.0353	0.0322	1
dwt (troy)	0.00343	0.00417	0.0549	0.05	1.555
grain (troy)			0.00229	0.00208	0.0648
1 carat * (troy) (1877)					0.2056
1 carat * (metric)					0.200
	Pennyweights dwt (troy)		Grains		Carats troy metric (1877)
1 lb (avoir.)	291.7		7000 (avoir.)		
1 lb (troy)	240.0		5760 (troy)		
1 oz (avoir.)	18.23		437.5 (avoir.)		
1 oz (troy)	20.0		480 (troy)		
1 g (metric)	0.643		15.45 (avoir.)		
1 dwt (troy)	1		15.43 (troy)	4.87	
			24 (troy)	7.57	
1 grain (troy)	0.0416		1 (troy)	0.3158	
1 carat * (troy) (1877)	0.132		3.168 (troy)	1	
1 carat * (metric)			3.086 (metric)		

* The carat as a unit of weight is sometimes found in old formulas, but is used nowadays only in connection with precious stones. Karat is generally used to express the purity of gold, e.g., 24 karat represents gold of the highest purity.

The factors²⁶ which govern the structure and color of gold deposits have been summarized as follows:

Physical Factors	Chemical Factors
1. Current density	6. Gold content
2. Agitation	7. Free cyanide
3. Temperature	8. Carbonates and other salts
4. Racking	9. Addition agents
5. Basis metal	10. pH
	11. Impurities

For most applications of gold plating (other than gold alloy plating), the color is more important than other physical characteristics. In general, the density and ductility of 24-karat gold deposits are satisfactory for most purposes. A bath for "bright" gold plating of thick deposits has not yet been achieved.

TABLE 3. DATA ON GOLD

Weight per Square Foot for Various Thicknesses

Inch	0.001	0.0001	0.00001	0.000001
Millionths of an inch	1000	100	10	
Ounces (troy)	1.465	0.1465	0.01465	0.001465
Ounces (avoir.)	1.607	0.1607	0.01607	0.001607
Pennyweights	29.3	2.93	0.293	0.0293
Grains (troy)	703.2	70.32	7.032	0.7032
Grams (metric)	45.57	4.557	0.4557	0.04557

1 grain (troy)/sq ft = 0.00000142 in. = 1.42 millionths of an inch

1 g/sq ft = 0.0000219 in. = 21.9 millionths of an inch

1 pennyweight/sq ft = 0.0000341 in. = 34.1 millionths of an inch

1 oz (troy)/sq ft = 0.000683 in. = 683 millionths of an inch

1 oz (avoir.)/sq ft = 0.000633 in. = 622 millionths of an inch

$$\text{g/l} \times 0.122 = \text{oz (troy)}/\text{gal}$$

$$\text{g/l} \times 0.134 = \text{oz (avoir.)}/\text{gal}$$

$$\text{g/l} \times 2.44 = \text{dwt}/\text{gal}$$

$$\text{oz (troy)}/\text{gal} \times 8.2 = \text{g/l}$$

$$\text{oz (avoir.)}/\text{gal} \times 7.5 = \text{g/l}$$

$$\text{dwt/gal} \times 0.41 = \text{g/l}$$

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Indium

HENRY B. LINFORD *

The chief application of indium plating is as a diffusion alloy in aircraft engine bearings. Smart¹ found that corrosion, due to oxidation products of the lubricating oil, of cadmium-silver-copper bearings was materially reduced by plating indium on the surface and then heat-treating it to diffuse it into the bearing alloy. For this purpose indium to the extent of 0.35% of the bearing alloy metal was used. It has also been demonstrated that similar results can be obtained by using 0.0001 in. of indium on lead-bearing surfaces, such as are used in aircraft.²

PRINCIPLES

In 1933 patents were issued to Gray^{3,4} and Murray⁵ which described a basic cyanide, dextrose-stabilized, plating bath. Westbrook⁶ studied the electrowinning of indium from sulfate solution. He found that a sodium citrate buffer was required, since insoluble anodes were employed. Fink and Lester⁷ gave the details of operation of indium sulfate bath using insoluble anodes. Linford⁸ gave details of the first soluble anode process for indium plating, using the sulfate bath. Other baths have been reported as follows: basic,⁹ fluoborate,¹⁰⁻¹² high pH cyanide,¹³⁻¹⁶ tartrate,¹⁶ perchlorate,¹⁷ and sulfamate.^{11,18} Of these baths the cyanide, high pH cyanide, sulfate, and sulfamate are the most important.

FUNCTIONS OF CONSTITUENTS OF BATH

In the cyanide and high pH cyanide bath the function of *d*-glucose is to complex the indium¹⁹ and thereby render it soluble in basic solution. That the cyanide is not necessary in the basic solution is evident from the composition of a basic bath,⁹ in which only indium, *d*-glucose, and sodium hydroxide are used. The simple cyanide bath is not stable, and a brown precipitate containing indium soon develops on

* Columbia University, New York, N. Y.

use. The addition of sodium hydroxide is said to help stabilize the cyanide bath.

The sulfate bath requires no addition agents for its operation, nor does the sulfamate; in these baths the anion simply acts as a convenient means of introducing indium, in a soluble form, to the bath.

OPERATING CONDITIONS

The operating conditions of the indium plating baths listed in Table 1 are given in Table 2. For the details of operation of the other

TABLE 1. FORMULAS

(a) Cyanide ⁴	In (as freshly ppt. hydroxide)	4-8 oz/gal (30-60 g/l)
	d-Glucose (at least $\frac{1}{2}$ weight of In)	2-4 oz/gal (15-30 g/l)
	NaCN	20 oz/gal (150 g/l)
(b) High pH Cyanide ¹⁴	In (as freshly ppt. hydroxide)	2-4 oz/gal (15-30 g/l)
	d-Glucose	2.7-4 oz/gal (20-30 g/l)
	KCN	19-21 oz/gal (140-160 g/l)
	KOH	4-5.3 oz/gal (30-40 g/l)
(c) Sulfate ⁸	In (as sulfate)	2.7 oz/gal or over (20 g/l)
	pH	2.0-2.7
(d) Sulfamate ¹¹	In (as sulfamate)	2.7 oz/gal (20 g/l)
	pH (adjusted with sulfamic acid)	0-0.2

TABLE 2. OPERATING CONDITIONS OF INDIUM BATHS

Bath	Amp/Sq Ft	Temp.	Anode	Current Efficiency
(a)	10-150	Room	Pt, graphite	50% variable depending on age
(b)	15-30	Room	Iron or steel	50% variable; not so dependent on age as bath (a)
(c)	20-40	Room	In	20-100% depending on pH, c.d., and cone.
(d)	20 opt. up to 100	Room	In	90%

indium baths mentioned under Principles, reference should be made to the original articles.

MAINTENANCE AND CONTROL

DETERMINATION OF INDIUM

The analysis of baths containing only indium can best be illustrated by outlining the procedure for analysis of the sulfate bath.

To 1 to 2 cc of plating solution add 0.5 g ammonium chloride and 100 cc water. Heat to boiling and add ammonium hydroxide to neutral, pH 7. Allow precipitate to settle at 50°C, then filter on ashless paper. Wash with normal ammonium hydroxide to which has been added 10% ammonium nitrate. Ignite below 700°C and weigh as indium oxide (In_2O_3).

For the basic and cyanide baths, complete removal of organics and cyanide must precede the precipitation of indium hydroxide.

pH

The pH of the acid baths must be controlled since the anode current efficiency is always at or over 100%, whereas the cathode current efficiency is nearly always considerably lower.

ANODES

The basic indium plating baths use insoluble anodes such as platinum, graphite, or iron. This is necessary because indium anodes polarize in these basic solutions.

Soluble indium anodes may be used in the acid solutions. Under these conditions the anode current efficiency always exceeds the cathode current efficiency, and it is therefore recommended that either a split anode circuit, using indium and platinum anodes, be employed, or that the pH be controlled by the alternate use of platinum and indium anodes.

PREPARATION OF BASIS METALS

The principal application of indium plating is for bearings. The steel shells have first a silver coating, either cast or plated onto them. They are then machined to 0.001 in. undersize on the radius. The lead plating which follows is done in a special jig to insure a central anode location, and therefore uniform lead plate. This plate is 0.001 in. thick. The bearing shell is then removed from the lead plating bath, rinsed, and immediately plated with about 0.0001 in. of indium. The indium is then diffused into the lead at about 175°C.

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Iron

C. T. THOMAS * AND V. A. LAMB †

Iron plating is one of the minor factors in the plating world. Although it made its appearance more than 100 years ago, electro-deposited iron has today few and limited uses. Much of the plating of other metals is done upon a base of iron or its alloys because of the deficiencies of iron in appearance and resistance to corrosion. Therefore, plating uses of iron are to be looked for in the deposition of heavy layers of metal, as in electroforming or electrorefining.

Although present applications of iron plating are limited, there is a continuing interest in electroforming with iron. Detailed instructions for operating the iron sulfate and the iron chloride baths are presented here, and several special purpose modifications of these baths that were developed during World War II are described.

HISTORICAL SURVEY

The electrorefining of iron has always been of interest in scientific circles as a means of securing metal of high purity for study of the properties of the metal as such or in alloys. Much of the literature on iron deposition deals with this phase of the subject, which has been comprehensively surveyed in a monograph.¹ Early commercial applications are also described in this monograph. These applications include production of iron electrotypes in Russia,² production of soft deposits³ used in Germany during World War I as a substitute for copper in driving bands for shells, production of iron sheets and tubes by electroforming,⁴⁻⁶ and building up of worn machine parts.^{7,8} Building up with iron plating is used today, but the field is limited and there is strong competition from both nickel and chromium. The good magnetic properties that can be developed in electrolytic iron⁹ led to its use by the Western Electric Company¹⁰ in Pupin induction coil

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† National Bureau of Standards, Washington, D. C.

cores prior to development of nickel-iron alloys with better magnetic properties.

An application in use today that recalls Klein's early work is a process reported in 1930¹¹ in which intaglio plates for printing government currency and bonds are made by depositing a nickel face backed by a heavy deposit of electrolytic iron from a hot chloride bath.

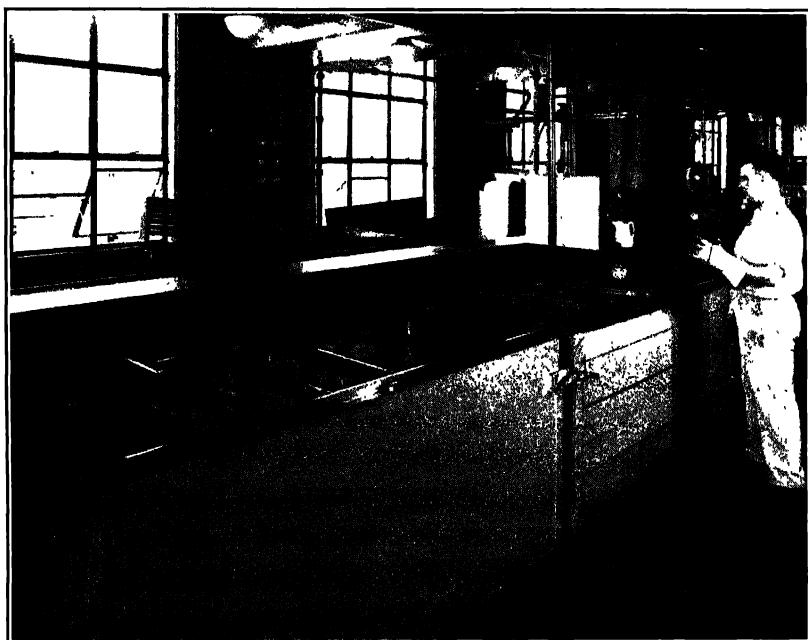


Fig. 1. Iron plating tanks for making currency plates at the Bureau of Engraving and Printing, Washington, D. C.

More recent work includes that done at the laboratories of the United States Rubber Company¹² on the electroforming of molds for rubber, glass, and plastics, and that done at the Mellon Institute¹³ on the production of iron powder for use in powder metallurgy.

World War II stimulated interest in iron plating as a means of saving nickel and copper in electrotyping and stereotyping, and three successful processes for this purpose were developed.¹⁴⁻¹⁶ Their use was not continued when nickel and copper again became readily available after the war, but it has been reported that the use of iron-plated stereotypes has been continued, e.g., for telephone directory plates.

Stoddard¹⁷ has recently reported a modified hot chloride bath for electroforming and building-up uses.

The fact that many of the commercial applications of iron plating mentioned above have been short-lived may seem discouraging, but there has always been a persistent interest which remains strong today. Iron is cheap and abundant, and it can be plated out in deposits possessing a variety of properties.¹⁸ It can be deposited as a hard and brittle metal which, by heat treatment, can be rendered soft and malleable. It can be deposited as a soft and ductile metal to which surface hardness can be imparted by the usual processes of carburizing, cyaniding, or nitriding. It welds readily, can be easily plated upon, and in the soft state has superior drawing properties.¹⁹ Recent observers agree that the deposited metal is more resistant to corrosion than other forms, as would be expected from its purity. The contrary opinion that has been widely quoted is probably due to failure to rinse completely free from traces of the electrolyte.

On flat or rounded surfaces that are not too deeply indented, deposits of any reasonable thickness can be made. In building up thick deposits from the chloride bath, it has been noted¹¹ that the grain growth becomes progressively coarser and the metal more brittle as deposition continues. To combat this, it may be found advisable to break up this grain growth periodically; for example, by interposing a deposited layer of another metal or by machining the surface of the deposit. The use of manganese chloride as an addition agent has been reported to reduce grain growth.¹⁷ The throwing power of iron plating baths is comparable to that of nickel baths.

It is not possible to enumerate the many small scale applications that are being carried on, but there is no question that these are increasing in number and interest.

PRINCIPLES

The ferrous sulfate bath, with or without added salts, was the first bath found practicable. In 1887 Alexander Watt²⁰ attempted to deposit iron from a large number of iron salts in solution and obtained deposits of some sort from many of them. His conclusion was that the solutions based on ferrous sulfate were the only ones of any practical value. However, more recent work indicates that iron plating solutions based on some of the less common salts, such as sulfamate²¹ and fluoborate,²² may have some merit. Working at or slightly above room temperature, Watt failed to obtain good deposits from chloride solutions, although Krämer²³ in 1861 had reported soft deposits from such a bath. With the later trend toward faster plating at higher temperatures, it was found that many baths based on ferrous chloride

are excellent media for electrodeposition at temperatures of 70°C or higher. Mixed baths containing both of these salts have been used. They may have some advantage for special purposes. This classification of iron plating baths into sulfate, chloride, and mixed sulfate-chloride types was made by Hughes,²⁴ who has probably done more work on this phase of the subject than anyone else. He states that the chloride bath has these advantages: the higher solubility of the salt permits the use of more concentrated solutions; the bath therefore has a higher conductivity, and higher current densities can be used than with the sulfate baths; the sulfate type of bath can be operated at much lower temperatures than can the chloride bath, and it does not oxidize so readily. Hughes further states that deposits from the sulfate bath oxidize much less quickly than those from chloride baths, an observation with which the writers do not agree, finding rather that both types of deposits rust somewhat less readily than does ordinary cold-rolled steel strip.

With both the sulfate and the chloride baths, a conducting salt, such as a corresponding alkali or alkaline-earth salt, is the most frequent addition. These salts may have effects on the properties of the deposits. The importance of the hygroscopic character of certain chloride combinations seems overstressed in the literature. Many other salts, such as those of various organic acids, have been recommended as ingredients of iron plating baths. These additions may be justified to meet individual needs, but for depositing soft and ductile metal simple bath combinations are recommended. Even in the case of the ferrous ammonium sulfate bath, analogy with the nickel sulfate bath would lead us to expect that the ammonium sulfate would cause harder deposits than could be obtained from the simple ferrous sulfate bath. For building-up purposes this added hardness may be desirable.

THE FERROUS SULFATE BATH

COMPOSITION AND OPERATING CONDITIONS

The sulfate type of bath is used principally for building up undersized machine parts. It has also been used in recent years for iron plating of stereotypes^{15, 16}. In this type of bath ferrous sulfate is the salt furnishing the metal. This salt may be used alone or with other salts added. Ammonium, magnesium, and sodium sulfates are the most common additions. The double salt, ferrous ammonium sulfate, seems to be used the most and to have been studied more thoroughly than other sulfate combinations. From the work of MacFadyen⁷ a

concentrated solution containing 47 oz/gal of ferrous ammonium sulfate operated at about 65 amp/sq ft with a temperature of about 60°C is recommended. MacFadyen kept this bath in a slightly acid condition, from 0.01 *N* to 0.02 *N* sulfuric acid. For operation at room temperature a current density of about 19 amp/sq ft is used. The bath may be operated at a low *pH*, for example 2.8 to 3.4, corresponding to an acidity of about 0.005 *N*, or at a high *pH* of 4.0 to 5.5. The covering power is better under the latter conditions, and the deposit is softer and under less stress. As with most simple baths, the conditions given may be varied widely, depending upon the results desired, provided that allowance is made for the interdependence of these conditions.¹⁸

MAINTENANCE AND CONTROL

In the low *pH* range the anode efficiency tends to be greater than 100%, and the cathode efficiency ranges from 80 to 90%. Sulfuric acid is therefore consumed and must be replaced by periodic additions to maintain the *pH*. In the high *pH* range anode and cathode efficiencies are close to 100%. However, air oxidation of ferrous sulfate followed by precipitation of ferric hydroxide results in a decrease in *pH*. The *pH* may be maintained by periodic addition of ammonium hydroxide, or by suspending ferrous carbonate in the bath. For best results the low *pH* bath should be kept fully reduced. In ordinary use any small amount of ferric iron will be reduced cathodically, but if a large amount is present it may become necessary to give the bath a reducing treatment, for example by addition of scrap iron in the presence of excess acid. In the high *pH* range any ferric ion that forms through oxidation is immediately precipitated as ferric hydroxide, so that maintenance of a reduced solution is automatic. However, the accumulated precipitate should be dissolved periodically by addition of excess sulfuric acid and reduced as described above. Wetting agents are helpful in these baths for control of pitting.

The iron concentration may be regulated by specific gravity measurements, with only an occasional analysis for iron. Routine methods of analysis for ferrous iron are satisfactory. Blum and Hogaboom²⁵ recommend titration with permanganate.

The acidity of the low *pH* solution can be measured by titration with dilute alkali. Colorimetric determination of *pH* can be used for either the low or the high *pH* solution. However, measurement of the *pH* with a glass electrode is recommended in both ranges because of its greater convenience and accuracy.

THE FERROUS CHLORIDE BATH

COMPOSITION AND OPERATING CONDITIONS

The most commonly used bath is the Fischer-Langbein solution,²⁶ which consists of a slightly acid solution of ferrous and calcium chlorides. Other alkali or alkaline-earth chlorides may be used in place of calcium chloride. The original formula, calculated in terms of concentrations,* is as follows:

Ferrous chloride, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	40 oz/gal (300 g/l)
Calcium chloride, CaCl_2	45 oz/gal (335 g/l)

For rapid deposition²⁷ a solution of ferrous chloride alone at a concentration of 54 to 67 oz/gal has been used. With either solution, ductile deposits are obtained at temperatures above 85°C. For average working conditions a cathode current density of about 60 amp/sq ft and a temperature of 90°C are used. The cathode current efficiency under these conditions is about 98%. The bath must be kept slightly acid by periodic additions of hydrochloric acid solution to maintain an acidity of about 0.01 N hydrochloric acid, or a pH of about 0.8 to 1.5 by glass electrode measurement. By operating at higher temperatures and acidities, good deposits can be obtained at current densities as high as 280 amp/sq ft.²⁷

World War II stimulated research in iron plating and led to published descriptions of several developments. In one of these it is claimed that a solution of the following formula¹⁷ yields deposits of finer grain size and permits a wider range of operating conditions than does the ferrous chloride-calcium chloride bath.

Ferrous chloride, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	27–66 oz/gal (200–500 g/l)
Manganese chloride, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	0.4–0.7 oz/gal (3–5 g/l)
Gardinol WA	0.13 oz/gal (1 g/l)
Temperature	70–105°C (160–220°F)
pH	1.5–2.5
Current density	50–300 amp/sq ft

The wetting agent, Gardinol WA, is used to reduce[†] pitting. It has been suggested[†] that the wetting agent may be largely responsible for the finer grain size of the deposit obtained from this bath.

Müller, Heuer, and Witnes²⁸ report that small amounts of chlorides of aluminum, beryllium, or Cr(II) added to a simple hot ferrous

* Reference 25, p. 360.

† Unpublished communication from W. A. Olson, Bureau of Engraving and Printing, Washington, D. C.

chloride solution render deposits softer and more ductile. The recommended concentrations are: AlCl_3 , 0.2–0.27 oz/gal; BeCl_2 , 0.67 oz/gal; CrCl_2 , 0.0013 oz/gal. Wallace and Iler²⁹ claim that 0.01 to 0.45 g/l of ferric ion in the hot ferrous chloride–calcium chloride bath results in a more uniform deposit, i.e., a better throwing power. The ferric ion concentration is controlled by means of an insoluble auxiliary anode.

MAINTENANCE AND CONTROL

The chloride baths described above should be maintained in the ferrous condition, although in the U. S. Rubber Company patent cited above²⁹ a small concentration of ferric ion is claimed to produce more uniform deposits. While more susceptible to air oxidation than the sulfate bath, when in operation the hot chloride type of bath is kept fully reduced by cathodic reduction, and when not in use stays in that condition for long periods, provided that the anodes are removed and a slight excess of acid is maintained. One author³⁰ has found that cubes of gum rubber floated on the surface of the bath do not interfere with its operation but serve as a cover which reduces oxidation, conserves heat, and keeps down evolution of steam and spray while the bath is working. A clear green color of the solution indicates that no harmful concentration of ferric salt is present, but a deepening yellow tinge or brown color shows an excessive content of Fe(III) . A reducing treatment as described for the sulfate bath, i.e., adding an excess of acid to act on anode scrap hanging in the bath, or operating with dummy cathodes, is then necessary.

As with the sulfate bath, control of the iron concentration by specific gravity measurement, with only an occasional analysis for ferrous iron, is sufficient. Titration with dichromate, using diphenylamine as an inside indicator, is a satisfactory method. The remarks on the measurement of the pH of the sulfate baths apply also to the chloride bath.

BATH IMPURITIES

For both types of bath, sulfate as well as chloride, the general statement may be made that organic impurities in solution cause brittle or cracked deposits. Not much is known concerning specific effects of inorganic contaminants. One of the authors in some unpublished work found that more than 0.2 g/l of zinc in the ferrous chloride–potassium chloride electrotyping bath caused excessive stress in the deposits. However, a small concentration of zinc apparently causes no harm in

the hot chloride bath.¹⁷ Stoddard¹⁷ cites low tolerance limits for copper, lead, arsenic, tin, and molybdenum in the hot chloride bath. In practice, no difficulty due to metallic impurities in this bath has been encountered.

SOLUTIONS DEVELOPED FOR APPLICATION TO ELECTROTYPING

A bath for the application of iron plating to electrotyping must give a relatively stress-free deposit at temperatures below the softening point of electrotyper's wax, e.g., about 35° to 40°C. With the more recent and growing practice of substituting plastic sheets for electrotyper's wax, higher temperatures can be used. A chloride type of solution that was used successfully for this purpose has the following composition and operating conditions:¹⁵

Ferrous chloride, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	32 oz/gal (240 g/l)
Potassium chloride, KCl	24 oz/gal (180 g/l)
Temperature	25–40°C (80–105°F)
Current density	20–50 amp/sq ft
pH	5.0–5.5

The pH is maintained by periodic additions of potassium hydroxide. A mixed sulfate-chloride type of solution was also developed for this purpose.¹⁶ The recommended composition and operating conditions are:

Ferrous sulfate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	33 oz/gal (250 g/l)
Ferrous chloride, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	5.6 oz/gal (42 g/l)
Ammonium chloride, NH_4Cl	2.7 oz/gal (20 g/l)
Temperature	40–43°C (100–105°F)
Current density	50–100 amp/sq ft
pH	4.5–6.0

Deposits from both of the above baths are brittle and must be backed with some copper to permit handling of the electrotype shell without breakage. Maintenance procedures for these baths are analogous to those for the high pH sulfate bath.

EQUIPMENT

All the iron plating solutions described above require acid-proof material for tanks and auxiliary equipment. Equipment similar to that used for acid pickling should be satisfactory. For most work,

rubber-coated steel tanks give good service. For heavy work, rubber-coated steel tanks lined with acid-proof brick are used. Duriron equipment for heating has a fairly long life. Glass, glass-lined, and ceramic equipment are very resistant to corrosion, but such equipment is hardly rugged enough for commercial use unless precautions are taken to protect the cell surface from thermal and mechanical shock. Where the heat developed from the passage of the plating current through the bath is sufficient, or nearly so, to maintain the proper working temperature, it has been found practical to inject live steam directly into the solution as the simplest means of initial heating. If there is too much condensate, closed coils of tantalum, silver, silver alloys, or impregnated carbon may be used. Lead coils may be used in the sulfate baths. In heating large circulating systems, alternating current between graphite anodes has been used, the plating bath being transferred to auxiliary tanks. If the nature of the work permits, mechanical agitation of the bath makes possible the use of higher current densities and facilitates the formation of a more even deposit.

ANODES

For both the sulfate and the chloride baths, anodes made of iron of high purity, such as ingot iron, wrought iron, or Swedish iron, are preferred. Steel and cast iron anodes have been used and when unbagged may be more satisfactory than pure iron anodes because smoother cathode deposits can be obtained. The presence of carbon in the anode reduces the likelihood of oxide being present, and this carbon remaining at the anode surface during corrosion of the anode seems to form a coating that retains particles that would otherwise lodge on the cathode surface and cause rough deposits. But, in general, it will be found necessary to bag the anodes. For this purpose, woven blue African asbestos has proved to be the most satisfactory material. The ordinary white asbestos deteriorates rapidly. Woven glass, though fragile, can be used and has been reported to be quite satisfactory when coated with a phenolic resin.¹⁷ The synthetic fabric Orlon, which has recently become available, is a satisfactory bag material. Porous stoneware diaphragms have been used but are rather cumbersome and have a relatively high electrical resistance. The necessity for bagging may be obviated by the use of continuous filtration. Iron anodes dissolve more readily than nickel anodes. No cases of passivity of iron anodes have been reported, even for high pH sulfate baths.

PHYSICAL CHARACTERISTICS OF DEPOSITS

A detailed account of what is known about the properties of electrolytic iron can be found in the monograph by Cleaves and Thompson.¹ From an engineering viewpoint, the mechanical properties are the most important. These vary widely, depending upon the bath composition and conditions of operation. For the metal as deposited, Kasper²⁷ reports a Brinell hardness number of 127 for a deposit made from a chloride bath at 93 amp/sq ft with a bath temperature of 102°C. For a deposit similar to this, Kasper reports a tensile strength of 61,000 lb/sq in. (4270 kg/sq cm) and an elongation of 18%. This agrees well with the data of Thomas and Blum,¹¹ who report a tensile strength of 56,000 lb/sq in. (4000 kg/sq cm) and an elongation of 20% for metal deposited from a chloride bath at a current density of 65 amp/sq ft and a temperature of 90°C. A deposit made at 186 amp/sq ft and 95°C had a tensile strength of 113,000 lb/sq in. (7910 kg/sq cm) and an elongation of 4%. Stoddard¹⁷ reports tensile strengths ranging from 47,500 lb/sq in. (3350 kg/sq cm) to 110,000 lb/sq in. (7760 kg/sq cm) with elongations of 50% and 10% respectively.

Deposits from the sulfate baths at or slightly above room temperature are harder than those from the hot chloride baths and have no measurable ductility. Schaffert and Gonser¹⁶ report Knoop hardness numbers * ranging from 160 to 780. The latter hardness appears to be extremely high compared with a maximum hardness number of about 350 Brinell reported by Maenaughtan¹⁸ for deposits from a bath of similar type.

Fusion or annealing of the electrolytic iron modifies the mechanical properties profoundly. After annealing at a temperature sufficient to cause recrystallization, i.e., at about 900°C, the mechanical properties approach those of open hearth ingot iron, with the strength approximating 40,000 lb/sq in. (2800 kg/sq cm) and the elongation 30 to 40%. The Brinell hardness number drops to 90 or lower. An annealing temperature of 500°C is sufficient to remove most of the effects of cold-working.

Lead

A. H. DU ROSE* AND WILLIAM BLUM†

The appearance and properties of lead limit its commercial use in electroplating largely to the field of corrosion protection. Its physical and chemical properties in this respect are such that it occupies a rather unique place among the metals. Although lead is attacked by the strongly oxidizing acids such as nitric and certain of the organic acids, notably acetic, lead coatings are fairly resistant to the non-oxidizing acids such as cold hydrofluoric and dilute sulfuric. When exposed in the air a slight film is formed on the surface which protects the underlying metal from further oxidation.

Lead has not been extensively electroplated because the low melting point of the metal (327°C) has made it possible to use a hot dipping process. For this process the lead must be alloyed with 2.5 to 20% tin, since molten lead does not adhere readily to iron. Recently, however, there has been a decided trend toward the use of electrodeposited lead for such applications¹ as the protection of metals from corrosive liquids like dilute sulfuric acid; lining of brine refrigerating tanks; plating of chemical apparatus; lining metal gas shells; barrel plating of nuts and bolts; plating storage battery parts; and plating apparatus used in the viscose industry. It has been pointed out² that lead plating is superior to lead dipping, as objects can be stamped and machined without distortion, the deposit is less porous, and, as shown by Kurlein,³ there is a minimum amount of stress present in electroplated lead coatings, whereas in dipped coatings there is a contractile stress representing about 3.5% shrinkage.

Lead has been deposited from a great number of different solutions:⁴ acid solutions of the nitrate, acetate,^{5, 6} fluosilicate, fluoborate, perchlorate,⁷ oxalate, dithionite,⁸ sulfonate,⁹⁻¹² sulfonates;¹³⁻¹⁵ and alkaline plumbites,^{16, 17} and cyanides from which immersion deposits can be

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† National Bureau of Standards, Washington, D. C.

obtained.¹⁸ Of these various baths the fluosilicate, fluoborate, and sulfamate largely form the basis of present-day lead plating.

The electrodeposition of lead from solutions of the fluorine acids dates back to 1886, when Leuchs¹⁹ first electrolyzed lead fluosilicate and lead fluoborate solutions. In 1901 Betts²⁰ secured a patent on the use of a fluosilicate solution similar in composition to the solution previously described by Leuchs. Later Betts²¹ patented the electrorefining of lead, using lead salts of fluorine acids with addition agents such as gelatin, "capable of restraining the crystallization of the deposit." Fluosilicate solutions have been extensively used for lead refining, but in ordinary plating operations they have occupied a place secondary to the fluoborate solution. The use of the fluoborate bath for lead plating came about largely as a result of studies made at the National Bureau of Standards¹ in 1918 on lead plating for military purposes. The perchlorate bath was patented by Mathers²² in 1909 and was reported to give excellent deposits of lead; however, it has been little used and has probably suffered because of the notion that aqueous solutions of perchlorates are explosive. Alkaline lead plating baths have not been used to any extent in this country, although the throwing power is reported to be superior to that of the acid baths.

There is a growing interest in electroplated lead coatings. With increased familiarity with present-day lead plating processes as well as with the development of new, improved processes, it is probable that in the future there will be many new commercial applications for lead plating, particularly for the protection of metals like copper and steel against certain acids, corrosive liquids and atmospheres, and as a substitute for more expensive and less available metals. Electroplated lead coatings have been proposed as a substitute for hot-galvanized coatings, especially when paint is to be subsequently applied. A preliminary report of the Wire Test Committee of the American Society for Testing Materials shows that, while lead-coated wires may show slight superficial rusting, the pores apparently become healed before structural corrosion of the iron occurs. Lead can be deposited as an alloy with many metals. Thus, by using the fluoborate solution it is possible to deposit alloys of lead and tin of excellent physical characteristics.²³ The possibilities of lead as an electrodeposited bearing alloy component have become evident.²⁴⁻³⁰ It is at least possible that lead plating may eventually find its widest application in alloy deposition processes.

The three lead plating baths used commercially are the fluosilicate, the sulfamate, and the fluoborate baths. The other proposed lead plating baths such as the acetate, perchlorate, dithionite, and alkaline

solutions have not reached the stage of wide commercial utilization. A comparison of the fluoborate and fluosilicate baths is given in Table 1.

TABLE 1

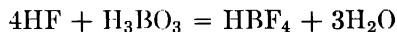
Bath	Advantages and Disadvantages
Fluosilicate	Difficult to prepare for small scale plating operations as contrasted with lead refining.
	Bath subject to decomposition, giving silica and lead fluoride.
	Cheaper for large scale operations. Will not plate directly on steel, requiring a preliminary coating of copper.
Fluoborate	Gives finer-grained, denser deposits than obtained from fluosilicate.
	Less susceptible to decomposition.
	More expensive than fluosilicate.
	Gives a satisfactory plate directly on steel.

FUNDAMENTAL PRINCIPLES OF OPERATION FOR COMMERCIAL BATHS

FLUOBORATE BATH

FUNCTION OF CONSTITUENTS OF BATH

When hydrofluoric acid and boric acid are mixed, it has generally been assumed that fluoboric acid is formed according to the equation



It is probable that the reaction is much more complicated and that the formula of fluoboric acid is more complex than HBF_4 . However, it has definitely been established that 4 moles of hydrofluoric acid react with 1 mole of boric acid to give an acid stronger than hydrofluoric acid, to which the formula HBF_4 has been assigned.

In the fluoborate bath, lead is present as lead fluoborate, usually denoted by the formula $\text{Pb}(\text{BF}_4)_2$. In practice, however, it has been noted that, when a solution normal in fluoboric acid is saturated with basic lead carbonate, the lead content of the solution is about 1.2 N, indicating that more lead is dissolved than corresponds to the formula $\text{Pb}(\text{BF}_4)_2$. This may be partly due to the known presence or formation of soluble hydroxyfluoborates.

The fluoborate bath is usually operated in the presence of some free fluoboric acid and a slight excess of boric acid over that required to react with the hydrofluoric acid. The presence of excess fluoboric acid

increases the conductivity of the solution and gives finer-grained deposits with less tendency toward treeing, probably because of the decrease in lead ion concentration brought about by the free acid. The presence of excess boric acid has little effect on the character of deposit produced, but it is desirable because it has been found to reduce the tendency for decomposition of fluoborate and subsequent precipitation of lead fluoride. There can be no appreciable excess of hydrofluoric acid in the solution over that required to form the fluoborate, since such solutions would produce a precipitate of lead fluoride.

BATH FORMULAS AND PREPARATION

As for other plating baths, the composition of the fluoborate lead bath varies, depending largely on the current density required. For deposits up to about 0.001 in. (0.025 mm) thick, produced at fairly low current densities, a bath of the following composition is recommended:

	Ounces per Gallon	Grams per Liter
Basic lead carbonate, $2(\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2)$	20	150
50% hydrofluoric acid	32	240
Boric acid	14	106
Glue	0.025	0.2

This gives a plating solution composition of

	Ounces per Gallon	Grams per Liter
Lead	16	120
Free fluoboric acid	4	30
Excess boric acid	1.8	13.3
Glue	0.025	0.2

For barrel plating operation or for still plating at higher current densities in which heavy deposits up to 0.05 in. (1.27 mm) thick are required, best results can be secured from a bath of the following composition:

	Ounces per Gallon	Grams per Liter
Lead	32	240
Free fluoboric acid	8	60
Excess boric acid	3.55	26.6
Glue	0.025	0.2

The fluoboric acid solution is best prepared by placing the necessary amount of commercial hydrofluoric acid in a lead-lined, rubber-lined, or wooden tank and slowly adding crystalline boric acid. Consider-

able heat is developed during the ensuing reaction. The solution is allowed to cool; then the lead is introduced as basic lead carbonate, in the form of a thick paste with water, added slowly with stirring. Considerable effervescence results from the dissolving of lead carbonate in the acid and the resultant evolution of carbon dioxide. The solution is then diluted to the required volume and decanted or filtered into the plating tank. Since the commercial materials used in the preparation of the solution invariably contain sulfate, some lead sulfate will be left behind in the original tank. The preparation of the fluoborate lead bath thus entails considerable care and caution, and differs from the preparation of most plating solutions in that the chemicals used must be added in a specific order. It is usually the practice to purchase a concentrated lead fluoborate solution which can be diluted to the required strength. Fluoboric acid can also be purchased.

OPERATING CONDITIONS AND CHARACTERISTICS

The acidity of the fluoborate bath is high enough so that the pH need not be controlled. However, the concentration of free fluoboric acid in the solution, although not critical, should be maintained within fairly definite limits.

The resistivity of the fluoborate bath as determined by Blum and co-workers¹ is:

Total Pb Normality	Total HBF ₄ Normality	Resistivity, ohm-cm
1.0	1.0	9.2
1.0	1.5	4.5
1.5	1.5	6.8
1.5	2.25	3.5
2.0	2.0	5.6
2.0	3.0	3.1

These data indicate that the fluoborate bath ranks among the highest conducting plating solutions, the exact value being a function of the amount of lead fluoborate and free acid present.

The commercial operating characteristics of the fluoborate bath are

Temperature	25–40°C (77–105°F); above 40°C (105°F) use cooling.
Cathode current density	<i>Dilute-type solution for thin deposits</i> 5–50 amp/sq ft, extreme limits. Average value, 20 amp/sq ft. <i>Heavy deposits, 10 amp/sq ft.</i> <i>Concentrated-type solution</i> 5–70 amp/sq ft, extreme limits. Average value, 30 amp/sq ft. <i>Heavy deposits, 20 amp/sq ft.</i>

Cathode current efficiency	100%
Throwing power	Haring cell, 1:5 ratio, 8 to 9%.
Anode current density	10-30 amp/sq ft.

MAINTENANCE AND CONTROL

The sludge formed in the fluoborate bath usually consists of lead fluoride or sulfate and can be removed by decantation or filtration. Copper can be removed by low current density electrolysis, and it has been reported³¹ that iron can be lowered to 0.4 g/l by the addition of fresh lead oxide to a pH of 3.4.

The chief constituents of the fluoborate lead plating bath are maintained by chemical analysis, and the addition agent is controlled by plating tests. The Hull cell³² may be effectively used to determine if sufficient glue or gelatin is present in the solution to produce the required grain structure and prevent undesirable treeing of deposits. The following procedure has been found satisfactory for the determination of lead in the bath:

1. A 10-ml sample is pipetted from the lead plating bath and diluted to 100 ml.
2. This solution is heated almost to the boiling point, and a slight excess of dilute 10 to 20% sulfuric acid is added.
3. The solution is allowed to cool and then is filtered on a prepared Gooch crucible. The precipitate is washed with a small amount of cold 4% sulfuric acid, dried, ignited at not over 600°C, and weighed.
4. Weight of precipitate multiplied by 9.1 equals ounces per gallon of lead; multiplied by 68 equals grains per liter of lead.

Many studies of the exact determination of free fluoboric acid and total fluoborate have yielded only unsatisfactory results, owing to the tendency of the acid to dissociate or hydrolyze upon dilution or standing. The following arbitrary method of control* has been developed and found satisfactory for maintenance of the bath:

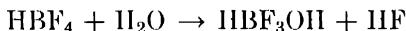
1. A 10-ml sample is pipetted from the lead plating bath and diluted to 250 ml.
2. The solution is titrated with standard 1*N* potassium hydroxide solution until the first permanent white cloudiness appears. This endpoint is taken to represent the free fluoboric acid in the solution. A fluoborate lead bath operating properly should require 4 to 6 ml of standard potassium hydroxide solution in this procedure. If the free acid is low as indicated by the titration, the bath is replenished by the addition of fluoboric acid. An abrupt increase in free fluoboric acid

* This method is described here with the permission of R. M. Drews, Republic Steel Corp., Upson Nut Division, Cleveland, Ohio.

usually denotes a decrease in the lead content of the solution, and it may be corrected by the addition of basic lead carbonate in the correct amount.

3. To the above aliquot solution are added 5 to 8 drops of phenolphthalein indicator, and the titration is continued to a permanent faint pink endpoint. This value is taken to represent the total fluoroborate content of the solution. Lead plating baths producing satisfactory results should require 26 to 30 ml of the standard 1*N* potassium hydroxide solution in this procedure.

The following method for free acid is believed to minimize the hydrolysis represented by the reaction



1. A 5-ml sample is pipetted into a 150-ml platinum or plastic dish.
2. To the sample is added 2 to 3 g of anhydrous sodium sulfate; this solution is stirred with a plastic rod to dissolve the salt and precipitate the lead.
3. One drop of methyl orange-cyanole indicator and 20 ml of ice cold water are added; this is titrated immediately with standard 0.5*N* sodium hydroxide to a greenish gray color, which is seen best after the lead sulfate is allowed to settle. The alkali consumed is due to neutralization of HBF_4 , HBF_3OH , and probably $\text{HBF}_2(\text{OH})_2$.
4. To calculate the acidity as HBF_4 , the following equation is used:

$$\text{ml alkali} \times \text{normality} \times 2.34 = \text{oz/gal HBF}_4$$

ANODES

Lead of satisfactory purity for anodes may be obtained either as "corroding lead" or "chemical lead." The objection to the presence of small amounts of insoluble impurities in the anodes is the formation of an anode sludge film, which causes an increased bath voltage. This sludge subsequently enters the plating solution and increases the tendency toward the formation of treed deposits. Anode corrosion in the fluoroborate bath is 100% efficient, and it is not necessary to add other anions to induce corrosion.

FLUOSILICATE BATH

FUN^TC_{ON}S_{OF}TS OF CONSTITUENTS OF BATH

Fluosilicic acid is formed by the action of hydrofluoric acid on silicon dioxide, which when treated with lead oxide yields the lead fluosilicate (PbSiF_6) electrolyte. Lead is present as PbSiF_6 , and the electrolyte

is usually operated with some free fluosilicic acid. The free fluosilicic acid may vary over wide limits and still produce satisfactory deposits, but in general it is maintained at 3 to 5%. Reeve³³ when plating army shell interiors and boosters, used a fluosilicate solution containing 18% of lead and 14% of fluosilicic acid, which when analyzed gave 2.9% free acid.

Although it is possible to secure smooth deposits of lead from the fluosilicate bath at low current densities, higher current densities tend to produce treeing, especially of heavy deposits. Therefore addition agents, most of which are colloidal materials or reducing agents, are always used. Glue is the most common addition agent in the fluosilicate bath. Reeve³³ found that, although the fluosilicate bath as received from the lead refineries ready for use in plating contained about 0.5 oz/gal of glue, the quality of deposit obtained was materially improved by the addition of another 0.7 oz/gal of glue. This was probably because the original glue had hydrolyzed and become ineffective. However, the use of too much glue in lead plating baths may result in the production of dark-colored deposits.

BATH FORMULAS

The fluosilicate bath recommended by Betts³⁴ contains about 8% lead and conforms to the following composition:

	Ounces per Gallon	Grams per Liter
Lead	10	75
Total fluosilicate	20	150
Glue	0.025	0.2

The proportions of lead and free fluosilicic acid may vary over wide limits and still permit the production of good deposits. The solution employed by Reeve³³ for plating shells had the following composition:

	Ounces per Gallon	Grams per Liter
Lead	24.0	180
Total fluosilicate	18.6	140
Glue	0.72	5.4

OPERATING CONDITIONS AND CHARACTERISTICS

The commercial operating conditions recommended for the fluosilicate bath are:

Temperature	35–40°C (95–105°F)
Cathode current density, extreme limits	5–80 amp/sq ft
Cathode current efficiency	100%

Tank voltage	0.1-0.2 v at 10 amp/sq ft
Anode current density	5-30 amp/sq ft

MAINTENANCE AND CONTROL

The fluosilicate lead bath is maintained by frequent analyses for lead and fluosilicate. The lead may be determined by the method described for the fluoborate solution. The free fluosilicic acid may be approximately determined by titrating an ice-cold solution sample with potassium hydroxide, using phenolphthalein indicator.³⁵ The total fluosilicate may be precipitated as the potassium salt, K_2SiF_6 , by the addition of a hot alcoholic solution of potassium acetate, or it may be determined by titrating with potassium hydroxide in a hot solution, using phenolphthalein as the indicator.

ANODES

"Chemical lead" or "corroding lead" anodes are commonly used in electroplating from the fluosilicate bath, and they show excellent corrosion characteristics. As with the fluoborate solution, impure anodes may cause a sponge to form on the anode surface, thus materially increasing the bath potential and influencing the character of the deposit produced as a result of sludge accumulation in the bath.

SULFAMATE BATH

CONSTITUENTS AND FORMULAS

The solution consists essentially of lead sulfamate, $Pb(SO_3NH_2)_2$, with sufficient sulfamic acid to give the solution a pH of about 1.5. Sulfamic acid became commercially available about 1938. Mathers,³⁶ Schweikher,¹⁰ Gray,¹¹ and Piontelli¹² have described the practical and commercial operation of the lead bath. The acid is stable and non-hygroscopic, and it may be considered a strong acid. As in other lead plating solutions, addition agents are needed to produce smooth fine-grained deposits.

Since both the acid and the salt are solids easily soluble in water, the bath may be prepared by adding the acid and salt singly or as formulated salts to water. The solution is made up concentrated enough to provide for operation over a wide range of current densities. The usual lead concentration may be between 15 and 22 oz/gal, and the pH about 1.5. As shown in Table 2, the lead concentration should be at least 15 oz/gal to avoid spongy deposits at the higher current densities.

TABLE 2.¹¹ EFFECT OF LEAD CONCENTRATION ON PLATING CHARACTERISTICS IN THE SULFAMATE LEAD BATH

Lead Concentration		Current Density Plating Range, amp/sq ft						
oz/gal	g/l	120	90	60	40	25	15	10
4	30	loose sponge	deposit	no deposit	
8	60	sponge	deposit	thin	
12	90	sponge	smooth lead deposit		
16	120	sponge	smooth, dense lead deposit	
20	150	smooth, dense lead deposit	
24	180	smooth, dense lead deposit	
		120	90	60	40	25	15	10

OPERATION AND MAINTENANCE

The bath requires very little attention except, as in other baths, to maintain the correct proportion of addition agents to produce the desired deposit. The operating characteristics are:

Anode efficiency	100%
Cathode efficiency	100%
Cathode current density	5-40 amp/sq ft
Temperature	24°C (75-120°F)
Throwing power (1:5 ratio)	About 0%
Resistivity	About 8.5 ohm-cm

The pH is easily controlled with sulfamic acid or ammonia and can be measured with a glass or quinhydrone electrode. A pH less than 1.5 or high temperatures will hasten the hydrolysis of sulfamic acid. The lead concentration can be controlled accurately enough by hydrometer readings with an occasional gravimetric analysis, and the Hull cell may be effectively used.

High purity lead anodes are recommended, although sludge from impure anodes does not cause significant roughness of the deposit. Anode slime may, however, cause an increase in voltage.

Acid-resisting tanks such as rubber-, brick- or asphalt-lined wood are used.

LEAD-TIN ALLOY PLATING

OPERATING CONDITIONS AND CHARACTERISTICS

It is possible to deposit from the fluoborate solution alloys of lead and tin²³ which are finer grained than either of the metals deposited under similar conditions. The process was discovered by Groff²⁷ while working on a satisfactory metallic coating for the inside of air flasks of naval torpedoes. The practice to be followed in the electrodeposition

of lead-tin alloys from the fluoborate bath is essentially the same as described for lead plating from this solution.

A tin fluoborate concentrate which can be purchased can be added to a lead solution to obtain the desired tin concentration, or the tin can be introduced into the bath by electrolysis of the lead solution with tin

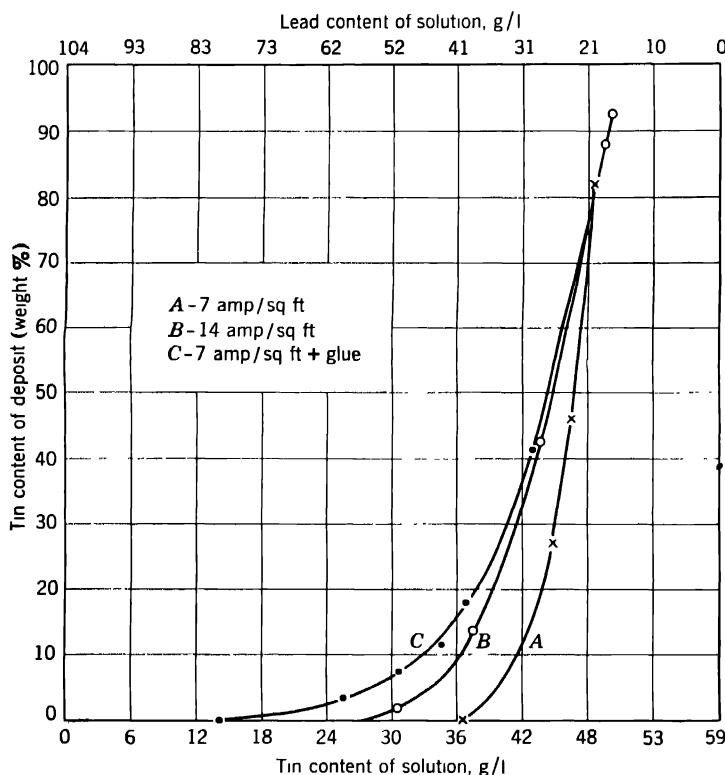


Fig. 1. Relative composition of lead-tin solutions and deposits.

anodes until the desired amount of tin as determined by analysis is present. Lead-tin anodes containing somewhat less tin than is desired in the deposit are generally used to simplify control of the tin concentration. Since the metal efficiency is 100%, it is possible to calculate the per cent of tin or lead in the deposit from the weight of the metal deposited and the ampere-hours.

The curve of Blum and Haring²³ shown in Fig. 1 gives the relation between the lead-tin ratio in the solution and the ratio of the metals in the deposit.

MAINTENANCE AND CONTROL

Within the range of 25 to 75 weight per cent of tin it is possible to produce continuous deposits of lead-tin having a composition which remains constant within a few per cent. By close control it is easily possible to produce alloy deposits of almost any composition. For bearings the tin content of the deposit is usually maintained at about 10%. For solderable coatings a higher tin content up to about 60% is used.³⁸ For alloy plating of bearings not more than 0.375 g/l of glue or greater than 12 amp/sq ft have been recommended.³⁹ This may have some relation to hydrogen embrittlement, since it has been shown⁴⁰ that the dilute lead fluoborate bath causes very little hydrogen embrittlement compared to other baths, including the more concentrated lead baths.

The analysis of the lead-tin bath is more difficult than that of the lead bath, especially for free acid. However, the procedures previously described for the lead bath can be applied for rough control of the alloy bath. Stannous tin can be analyzed by the usual iodine method.

The following method for determining the deposit composition is based on determining accurately the weight of a given tin-lead alloy deposited by an accurately determined number of ampere-hours. The weight of deposit can be determined by weight difference, i.e., by weighing a small cathode before and after plating. The ampere-hours can be determined by a calibrated ammeter and stop watch (with a steady, unvarying current) or a coulometer. The coulometer can be a lead plating cell in series with the alloy solution cell. The alloy solution cell can be the alloy plating tank. Let W = the weight of alloy deposited, in grams; let A = the number of ampere-hours to deposit W ; let X = fraction of lead in the deposit. $1 - X$ will equal the fraction of tin in the deposit. $100X$ equals the per cent lead in the deposit. Then

$$X = 2.341 - \frac{5.182A}{W}$$

ADDITION AGENTS

Since there is very little necessity for bright lead or lead alloy deposits, not a great deal of study has been devoted to addition agents for lead baths. The suppression of treed and very coarsely grained deposits obtained without addition agents and an increase in throwing power and covering power are usually all that is required, and this is easily accomplished by common addition agents. In many cases the

same addition agents which have been found effective for acid tin baths are even more effective for lead baths; they may even be too effective in that they cause very fine powdery deposits. Materials such as glue or gelatin are most generally used. Betts²¹ has suggested gelatin, pyrogallol, resorcinol, saligenin, *o*-amidophenol, and hydroquinone as suitable addition agents in depositing lead from a fluorine acid salt solution. Blum and co-workers¹ found the effects of glue and gelatin in the fluoborate bath under similar conditions to be the same; i.e., there is less tendency for the lead deposit to form trees, and plates of a given thickness are finer grained and more nearly impervious. In commercial operation occasional small additions of glue are made whenever the deposits show a tendency toward roughness or treeing. In small scale experiments it has been found that over 800 g of lead could be deposited from 1200 ml of fluoborate solution containing 0.2 g/l of glue before treeing became evident,¹ and even after this period of operation the effect of glue was still noticeable in that the tendency toward treeing was less pronounced than in a solution to which no glue had been added.

Anthraquinone sulfonate¹¹ and polyethers⁴² such as β -naphthol, polyethylene oxide, and Carbowax have been found effective for sulfamate and fluoborate solutions. A few systematic studies^{43, 44} on the effect of wetting agents and surface-active compounds on polarization and structure of lead deposits have been made.

Rosin¹⁶ and quaternary ammonium compounds¹⁷ have been used for alkaline lead solutions with the addition also of rochelle salts to aid in anode corrosion.

Glue (or gelatin) and resorcinol are commonly used in the lead-tin fluoborate solutions. These agents not only promote smooth deposits but also increase the tin content of the alloy for a given solution composition.^{45, 46}

PREPARATION OF BASIS METAL

The cleaning procedure found satisfactory for ferrous materials, such as nuts and bolts that are to be barrel plated with lead, consists of a thorough electrolytic cleaning in the ordinary type of alkaline cleaner followed by a short pickle or dip in 5 to 8% sulfuric acid or 20% muriatic acid.

In still plating it is often advisable to use sand or "steel shot" blasting instead of pickling; this is essential if the lead deposits are subsequently required to withstand elevated temperatures. Pickling in either hydrochloric or sulfuric acid should continue for only a

short time, as this pickling period appears to be related to adequate adhesion of the lead plate. Even though lead can be directly deposited on iron and steel from the fluoborate bath in a condition satisfactory for many purposes, it has repeatedly been found desirable to use a preliminary cyanide copper strike. Removal of the fine deposit of sand from the iron surface after sand blasting is important. Even a sulfuric acid pickle at times does not dislodge all the silica from the pores of the metal surface. "Steel shot" cleaning is preferred. The copper strike is especially advantageous if the steel or cast iron surface is rough, since the covering power of the copper is better than that of lead and the covering power of lead on copper is better than that of lead on iron.¹⁵

CORROSION RESISTANCE AND TESTS OF DEPOSITS

Freedom from porosity rather than actual thickness of the deposit is in a large part the criterion for the protective value of lead deposits. May¹⁷ has reported that lead deposits protect iron and steel from corrosion indefinitely if they are at least 0.0008 in. (0.02 mm) thick. Kurrein³ has stated that a thickness of 0.0001 to 0.0002 in. (0.0025 to 0.0051 mm) of electroplated lead is sufficient to pass a porosity test. However, it must be remembered that lead is a soft metal and, if exposed to any abrasion or wear, a coating of this thickness will soon disappear. In any case, the exact thickness of lead required to give an impermeable coating will depend upon the smoothness and cleanliness of the initial surface and upon the structure of the lead deposit. Blum and co-workers¹ state that from solutions containing glue a thickness of 0.003 in. (0.076 mm) is sufficient for severe service, but 0.005 in. (0.127 mm) is recommended. With light coatings a slight burnishing or even scratch-brushing will render the coating less porous. Lead-plated nuts and bolts usually have a thickness of 0.0005 to 0.001 in. (0.0127 to 0.025 mm). Most ferrous metals are plated with a thickness of 0.0005 to 0.008 in. (0.0127 to 0.2 mm), depending on the subsequent exposure of the plate. If the lead coatings are to withstand severely corrosive liquids at elevated temperatures, as in certain chemical apparatus, deposits of 0.05 in. (1.27 mm) or more may be required.

The recently published results of corrosion tests⁴⁸ of lead on steel by A.S.T.M. give the following generalizations on lead as a protective coating for steel:

1. There is a wide variation in the protective value of lead coatings. The coatings are more protective at New York (industrial atmos-

sphere) than at Kure Beach (seacoast atmosphere), with intermediate effectiveness in rural and semi-tropical atmospheres.

2. There is a similar variation of the corrosion rate of lead itself.

3. The rate of corrosion of bare steel in different atmospheres does not seem to be related to the corrosion protection offered by lead to steel.

4. A copper flash undercoating is beneficial for the thicker lead deposits but accelerates steel corrosion for the thinner deposits. The critical lead thickness depends on the atmosphere and the corrosion rate of lead.

It is obvious that the corrosion rate of lead itself and the corrosion products of lead are important in the protection offered by lead to steel. Because in some atmospheres the corrosion products fill and close up the pores, it is difficult to evaluate the extent of sacrificial protection offered by lead to steel. Lead coatings do seem to have a tendency to protect steel electrochemically in seacoast atmospheres,⁴⁹ but it would appear that the protective and pore-sealing properties of the corrosion products are of greater importance, especially where the corrosion products are formed in an industrial atmosphere. As would be expected, the coarse crystalline deposits obtained from baths with no addition agent do not have as much protective power as the smoother deposits from solutions containing addition agents. It has also been reported⁴⁵ that deposits containing 5 to 6% tin have better corrosion resistance than deposits containing either less or more tin, especially as shown by the salt spray test.

Although the salt spray test may be of doubtful value except to show gross imperfections, emergency specifications have been issued.⁵⁰ These requirements are easily met by good lead deposits on smooth steel surfaces.

A rapid test for porosity of lead deposits may be made by a modification of the ferroxyl test. The samples to be tested are washed in 10% sulfuric acid to remove superficial particles of iron or iron oxide derived either from the solutions or from dust in the air, and are then treated with a solution containing 2.7 oz/gal of sulfuric acid and 1.3 oz/gal of potassium ferricyanide. The presence of pores in the deposit is indicated by the appearance, within a minute, of bright blue spots.

The Brenner Magne-Gage has been found satisfactory for determining the thickness of the lead coating. Another method involves the mounting of the specimen in some plastic material, such as lucite or bakelite, and measuring the thickness of the deposit under the microscope. However, with this method it is possible that the pressure used

in mounting the specimen may distort or compress the layer of electro-deposited lead. Still another method is the dropping or jet test,^{51, 52} using a solution of acetic acid and peroxide.

STRIPPING OF LEAD AND LEAD-TIN DEPOSITS

The following solutions have been used with success for stripping lead or lead alloys from steel:

A. ⁵³	Sodium hydroxide	13.3 oz/gal (100 g/l)
	Sodium metasilicate	10.0 oz/gal (75 g/l)
	Rochelle salts	6.7 oz/gal (50 g/l)
	Temperature	82°C (180°F)
	Work as anode at	20-40 amp/sq ft
B.	Sodium nitrate	67 oz/gal (500 g/l)
	pH	6-10
	Temperature	21-82°C (70-180°F)
	Work as anode at	20-200 amp/sq ft
C.	Immersion in	
	Acetic acid	10-85% by volume
	Hydrogen peroxide (100 vol.)	5% by volume

Method C, at 16°C, will strip 0.001 in. of lead in 6 or 7 min with very slight etching of the steel. Methods A and B will strip at the 100% theoretical rate. With method B the voltage will increase quite suddenly when the lead coating has been removed. For instance, at room temperature and 100 amp/sq ft the voltage may be about 2.7, but it jumps to 4.6 v when the stripping is complete. With this solution there is very little consumption of nitrate because the lead in solution hydrolyzes and precipitates.

Occasionally, with solution A or B a stain remains on the steel after stripping. This can be removed by a half minute immersion in solution C, which leaves the steel perfectly clean and unetched (unless the voltage in the nitrate solution was lower than about 2 v).

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13.

Nickel

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Nickel plating is used primarily to protect metallic objects from corrosion, especially steel, brass, and zinc die castings and, to a smaller extent, aluminum and magnesium alloys. Good appearance is usually important, and therefore non-tarnishing chromium is usually applied on top of the nickel. Less frequently, gold or brass with a lacquer finish is used as a final coating. On account of its mechanical properties, nickel plating is used to some extent to repair worn parts, and for electroforming of printing plates, phonograph masters, sheet, tube, screen, and many other articles.¹

The history of nickel plating goes back over one hundred years. It began in 1843 when R. Boettger (or Boetcher) described the first apparently sound nickel plate, which he obtained from a bath containing nickel sulfate and ammonium sulfate. Following the lead of Roseleur in 1849, Adams² in 1869 was probably the first to do nickel plating on a truly commercial basis. He too used double salt baths, including both sulfate and chloride baths, but so prepared as to be neutral and free from harmful impurities.³ He also introduced the first soluble anodes which contained iron and carbon.⁴ Many bath compositions were proposed up to 1913, as shown in Watts' paper, "Electro-deposition of Cobalt and Nickel."⁵ However, the only early developments which have survived are: Weston's invention of the low voltage d-c generator in 1874, and his introduction of boric acid into the nickel bath;⁶ the use of chlorides by Bancroft⁷ and others to promote anode corrosion; and the discovery in the Elkington plant of Birmingham, England, in about 1912, that cadmium salts act as brighteners. Notable also is the observation that the higher metal content obtained

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by adding nickel sulfate to the nickel ammonium sulfate solution was desirable in many instances. Electrolytic nickel refining profited by the experience of the nickel plater and has made use of warm nickel sulfate-boric acid solutions since 1894.

The rate of development has been quite rapid since 1915. Among the mile posts along the road the following should be mentioned: high speed plating, begun by Watts with his famous "Watts bath";⁸ control of quality of deposits, first emphasized by Watts and DeVerter⁹ and finally maturing into American Society for Testing Materials-American Electroplaters' Society specifications in 1935; accurate pH control,

TABLE 1. SUMMARY OF AMERICAN SOCIETY FOR TESTING MATERIALS-AMERICAN ELECTROPLATERS' SOCIETY SPECIFICATIONS

Basis Metal	Service *		
	Severe *	General *	Mild *
Steel	Type D.S.	Type F.S.	Type K.S.
Cu + Ni, min.	0.0020 in †	0.00125 in.	0.00075 in.
Final Ni, min.	0.0010 in.	0.0006 in.	0.0004 in.
Cr, if required, min.	0.00001 in.	0.00001 in.	0.00001 in.
Salt spray ‡	96 hr	72 hr	48 hr
Zinc	Type F.Z.	Type K.Z.	Type Q.Z.
Cu + Ni, min.	0.00125 in.	0.00075 in.	0.0005 in. §
Cu, min.	0.0004 in.	0.0003 in.	0.0002 in.
Final Ni, min.	0.0005 in.	0.0003 in.	0.0003 in.
Cr, if required, min.	0.00001 in.	0.00001 in.	0.00001 in.
Salt spray	48 hr	32 hr	16 hr
Copper	Type F.C.	Type K.C.	Type Q.C.
Ni, min.	0.0005 in.	0.0003 in.	0.0001 in.
Cr, if required, min.	0.00001 in.	0.00001 in.	0.00001 in.

* Terms not used in the specifications.

† When copper is used in excess of 0.0001 in., its minimum thickness should be 0.00075 in.

‡ Continuous, 35°C (95°F), 20% NaCl spray operated in accordance with A.S.T.M. Designation B 117-49T.

§ Total of 0.0003 in. if no copper is used.

|| To prevent cracking of the chromium, the minimum should be deposited with a maximum of less than 0.00005 in. chromium.

introduced by Thompson;¹⁰ low *pH* baths, suggested by Phillips;¹¹ commercial introduction of modern bright nickel plating begun by Schlötter¹² and the many later developments of it; design of baths for deposition of easily buffed, semi-bright nickel coatings; growing appreciation of the importance of high purity electrolytes and of high ductility of and low stress in deposits; and development of automatic and highly improved polishing, buffing, and plating equipment that makes possible today's high production rates and low costs.

It is difficult to predict what the future will bring in the way of further development, but one may expect decided progress in bright and semi-bright nickel plating with deposits of higher protective value and greater ability to hide basis metal imperfections. The application of periodically reversed current of high frequency to nickel baths containing only inorganic addition agents offers promise in both directions.

SELECTION OF ELECTROLYTES FOR DECORATIVE PLATING

The number of different solutions successfully used today is legion; however, they can be easily classified into a limited number of types.

The double nickel salt bath, with low nickel content and containing substantial amounts of ammonium salts, and the high sulfate nickel bath for plating on zinc and zinc alloys have both become almost obsolete.

The complex ammoniacal pyrophosphate-citrate bath, containing bisulfite,¹³ was especially designed for plating on zinc and its alloys. It has unusual ability to cover recesses without streaking but produces nickel coatings that contain much basic material and is seldom used for specification work.

The Watts bath⁸ is of paramount importance, because it is the basis of most modern baths used to apply decorative coatings, bright and semi-bright, and produces some of the deposits employed for engineering purposes. It originally contained 32 oz/gal $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 2.7 oz/gal $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 2.7 oz/gal H_3BO_3 . At present the chloride content is at least tripled, and the boric acid content approximately doubled. This solution is operated at elevated temperature and is capable of being used with high current densities. By the addition of other ions and by control of plating conditions, the nickel deposit can be had in various degrees of hardness, tensile strength, and elongation to meet special mechanical requirements.¹⁴

Considerable interest is shown in the all-chloride bath developed by Blum and Kasper¹⁵ and by Wesley and Carey,¹⁶ with its very high conductivity and high anode and cathode efficiencies. The better-buffered half-chloride, half-sulfate bath of Pinner and Kinnaman¹⁷ has most of the advantages of both the Watts and the high chloride baths and has been found to be especially suitable for high speed production.

The types of nickel plating baths most commonly used today are the bright and the semi-bright nickel baths. Both are modified Watts baths, ordinarily containing 10 to 12 oz/gal of nickel to which have been added certain addition agents.

The modern bright nickel differs from the old-fashioned bright deposits in that it can be applied in any thickness, with or without subsequent chromium plating, and without blistering, exfoliation, or cracking. Furthermore, the luster is much more intense, and the plate often exhibits a greater smoothness than the underlying basis metal or pre-coating. Finally, the modern bright plating baths are high speed baths.

The smoothing effect is not sufficiently pronounced that the underlying surface can be ignored. The required smoothness of this surface depends on the requirements for the appearance of the finished plated article. This, in its turn, depends on several factors. Parts which are viewed from afar need a less perfect finish than those which are seen from a short distance. Flat or slightly curved surfaces show up imperfections (including polishing lines) much more than do parts with a surface broken by the design or having areas of small radii. These factors become progressively less important as the thickness of the bright nickel coating increases.

How these considerations affect the polishing and plating practice is discussed in detail on pages 332 to 336. With few exceptions, bright nickel can be used to advantage as long as its relatively high brittleness does not preclude its use and properly designed preparatory cycles are employed. Included in the latter are: proper dies for forming the basis metal; suitable preparation of the basis metal by polishing or buffing or both; and, when required, a smooth, non-grainy or a buffed copper undercoating.

Semi-bright nickel coatings must be buffed to get a mirror-like luster. Buffing of such coatings removes less of the plate and, therefore, is accompanied by less decrease in corrosion resistance than when dull nickel plate is buffed. Bright nickel coatings ordinarily are not buffed unless the bath is out of balance, the racking is below standard, or polishing marks or other surface imperfections are to be hidden. In such cases, relatively light color buffing is used, which removes little

or no nickel. An undercoat of copper is sometimes used over imperfect steel surfaces to reduce the buffing cost. Overall economy may be thus effected.

PRINCIPLES

THE WATTS BATH

Anyone who wishes to understand modern nickel plating as practiced in the United States and Canada must first familiarize himself thoroughly with the Watts bath and the effects of all controllable variables upon the properties of the deposits made from this type of electrolyte. In actual tonnage of nickel deposited per year the bright and semi-bright nickel baths are of predominant importance, but they all include the basic Watts ingredients. Where other ingredients are used in commercial baths, they are used for very specific purposes which will be discussed later.

The fundamentals of nickel plating are to be observed in the effects of such variables as temperature, nickel concentration, current density, pH, and agitation upon deposits from the Watts bath. This bath opened the way for rapid plating at elevated temperatures. This improvement was, in a large part, due to bath composition and operating conditions favoring a rich and constantly replenished cathode film and high anode efficiency. The modern Watts formula is more concentrated than the original. A survey of recent information shows that it can be represented reasonably well by the following:

Nickel sulfate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	40 oz/gal (300 g/l)
Nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	8 oz/gal (60 g/l)
Boric acid	5 oz/gal (38 g/l)

FUNCTIONS OF CONSTITUENTS

NICKEL SULFATE

In the Watts bath the major part of the nickel ion content is contributed by nickel sulfate. This salt is used because it is the least expensive salt of nickel with a stable anion that is not reduced at the cathode, oxidized at the anode, or volatilized. Sulfates are also less corrosive than chlorides and some other salts of nickel. The limiting cathode current density for sound nickel deposits is a function of the nickel ion concentration in the cathode film, which in turn is dependent on the metal ion concentration of the bath itself. The larger amount of nickel sulfate now used in the Watts bath not only raises the limit-

ing cathode current density but also lowers the resistivity of the bath which reduces power costs and improves plate distribution.

CHLORIDE ION

Chloride ions are now introduced by adding nickel chloride instead of sodium chloride to simplify the composition and control of the bath and to avoid secondary effects such as an increase in stress of deposits ascribed to the presence of sodium ions.

A principal function of the chloride ion is to improve anode dissolution by reducing polarization; it also has marked effects at the cathode. They are at a maximum in the all-chloride bath studied in detail by Wesley and Carey,¹⁶ who listed its advantages and disadvantages. The advantages include: higher permissible cathode current density; smoother, finer-grained, harder, and stronger deposits; less tendency to form pits, nodules, and trees; and increased throwing power resulting from increase in cathode efficiency, electrolyte conductivity, and slope of the cathode potential curve.¹⁸ Disadvantages are: greater corrosiveness of the electrolyte, which prevents the use of lead tank linings and coils; more rapid rise in pH during use; lower ductility of deposits; and increase in stress, which will be discussed later. A high speed nickel plating bath was developed by Pinner and Kinnaman¹⁷ which contains chloride and sulfate in about equal normalities to combine the advantages of high chloride with a minimum degree of the disadvantages. This bath will be further discussed under heavy nickel plating.

Graham, Heiman, and Read¹⁹ indicated the importance of the chloride ion when they showed that a reduction of its concentration is the most profound change taking place in the cathode film during nickel plating, and that its effect upon precipitation of colloidal matter may be associated with burning.

BORIC ACID

In the absence of a buffer, nickel deposits at ordinary temperatures are prone to be hard, cracked, and pitted as shown by Macnaughtan.²⁰ Yet Blum and Kasper²¹ made excellent heavy deposits from unbuffered boiling electrolytes. There are special purpose commercial baths which utilize buffers other than boric acid, but the latter is generally preferred because it is obtainable in a very pure and inexpensive form, is relatively non-volatile and stable, produces whiter deposits, and is helpful in its smoothing action on the plate. Its concentration is not critical in the Watts bath.

ADDITION AGENTS

The only common addition agents in the Watts bath are employed to prevent pitting. Wetting agents are used exclusively for this purpose in bright nickel plating baths and may be used in the Watts bath in the same way, as discussed on pages 317 and 318. One disadvantage in using wetting agents is that oil or grease dropped on the bath becomes emulsified, has a harmful effect upon the ductility of the deposit, and may be the cause of a serious outbreak of pitting. Decomposition products of wetting agents may also accumulate in time and have a similar effect until the bath is purified.

Where the highest ductility is required or when other physical properties must be rigidly controlled, hydrogen peroxide is used as needed to prevent hydrogen pitting. It operates by depolarization of the cathode, as well as by oxidation of ferrous iron and decomposition of undesirable organic contaminants of the bath. The amount of peroxide required to prevent pitting is a function of bath purity. The usual recommendation for a Watts bath is an addition, once a day, of 1 part of 30% hydrogen peroxide per 2000 parts of solution. A grade free of organic stabilizers should be used. Localized additions of peroxide next to the cathode should be avoided; instead it should be added in a manner favoring its intimate and complete mixture with the whole electrolyte. By frequent analysis and additions, a constant concentration of hydrogen peroxide has been successfully maintained in a large scale nickel plating plant with uniformly good results. The rate of decomposition of peroxide increases rapidly with increase in *pH*; ²² hence this addition agent is more efficient in low *pH* than in high *pH* baths. An excess of hydrogen peroxide is to be avoided, because it increases the contractile stress in the deposit, and, in still larger amounts, causes burning and embrittlement.

Other oxidizing agents are used occasionally: for example, sodium perborate, which decomposes to form hydrogen peroxide; and nitrates, which have been employed in France. In England it is rather common to add the chloride ion as potassium chloride, which is said to reduce incidence of pitting, at least under the conditions of the moderate current densities and temperatures employed there.

American nickel plating baths commonly contain a small amount of cobalt derived from the anodes and salts. This fractional percentage of cobalt is considered to have no significant effect upon the properties of the deposit. Experimental work which confirms this point has been completed in one of the research projects of the American Electroplaters' Society.²³

COMPOSITION RANGES

The above discussion of the functions of the ingredients of a Watts bath shows that the concentration can be varied over a rather wide range. The typical formula is excellent for an average cathode current density of 50 amp/sq ft at a temperature of 50°C. Under such conditions local current densities of one-half or twice this value will still result in excellent plating. If one wishes to plate at a lower average current density, for example at 20 amp/sq ft, the nickel sulfate and nickel chloride contents may be halved. For higher current densities than normal, the salt concentrations can be increased, but the practical difficulty of excessive drag-out losses and crystallization limits changes in this direction. Current densities higher than 100 amp/sq ft are better achieved by increase in agitation, temperature, and ratio of chloride to sulfate as previously shown.

EFFECTS OF OTHER CONTROLLABLE VARIABLES

Other factors, like the electrolyte composition, also influence the nature of the cathode film and thereby the quality of the deposit. They are current density, temperature, pH, and degree of agitation or relative motion of cathode and solution. They are all interrelated, and to the extent that, if a variable such as current density is altered considerably without the other factors being altered at the same time, adverse effects upon the cathode deposit may be noted. For example, the typical modern Watts bath can be operated at 54°C and pH 2.0 to give sound, ductile gray deposits at 60 amp/sq ft with a moderate degree of agitation. If the current density is lowered to 2 amp/sq ft without reduction of the temperature or increase of the pH, bright brittle deposits will be obtained.

The relation between limiting current density, temperature, and pH in a bath of the original Watts composition (32 oz/gal nickel sulfate, 2.7 oz/gal nickel chloride, and 2.7 oz/gal boric acid) was determined by Phillips¹¹ and is summarized graphically in Fig. 1. Similar data are not available for more concentrated Watts solutions, but for them the limiting curves of Fig. 1 would be displaced to the right. The curves would also be displaced to the right for increasing rates of agitation of the electrolyte over the cathode surface.

Phillips' work showed that the range of permissible current densities is greatly extended at low pH, where smoother deposits are obtained because of the greater solubility of metallic impurities. Disadvantages of lowering the pH too far will appear in the later discussion

of current efficiency and throwing power. A bath operated in the pH range of 1.5 to 2.0 is sometimes used for an original flash nickel coating for the purpose of producing a smooth, adherent, rather lustrous base plate.

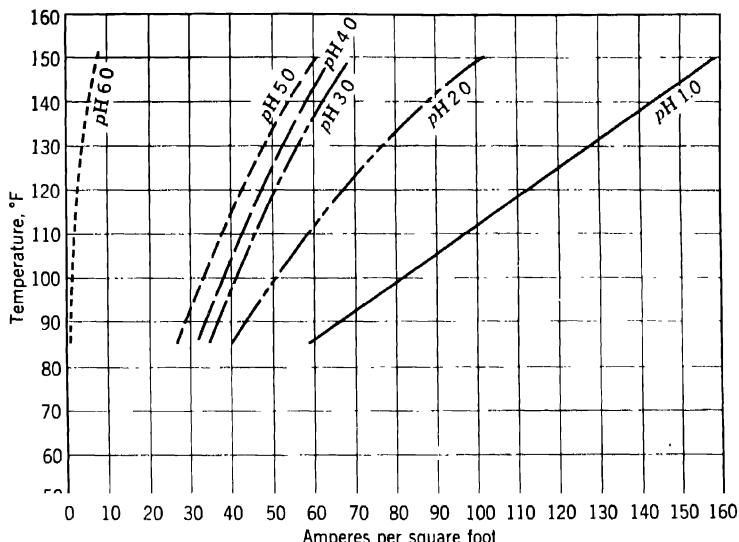


Fig. 1. Plating ranges of Watts bath for 0.0005-in deposits according to Phillips.¹¹ The area to the right of any given line is the area of burned and peeled deposits at that pH when the deposit is 0.0005 in. thick. The area to the left of any given line is the area of good deposits for that pH.

METAL DISTRIBUTION (THROWING POWER)

As discussed in Chapter 1, the electrochemical properties which determine metal distribution over a cathode of a given shape are cathode polarization, solution conductivity, and cathode efficiency. A large slope of the cathode potential-current density curve, a small or negative slope of the cathode current efficiency-current density curve, and a low specific resistivity of the electrolyte favor more uniform metal distribution or higher throwing power. How these characteristics of a Watts bath are affected by changes in the plating variables will indicate the probable effect of these variables upon throwing power.

The specific resistivity of the Watts bath is about 11 ohm-cm at 60°C, and it decreases in the usual way with increase in temperature.²⁴ It also decreases with increasing total concentration²⁴ and increasing chloride ion concentration¹⁶ of the bath. It is but little affected by pH within the range 2.0 to 5.5.¹⁸

Like the cathode efficiency of all nickel plating baths, that of the Watts bath rises with increase in current density until the limiting current density is reached. It also rises with increase in temperature and with total concentration.^{24,25} Increase in chloride ion concentration has a more markedly beneficial effect, but the effect of pH is most pronounced. The current efficiency decreases rapidly with a fall in

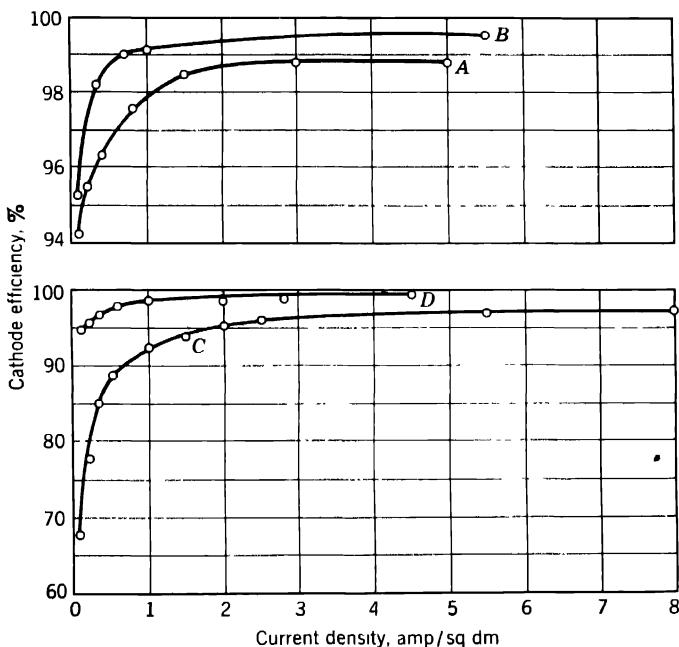


Fig. 2. Typical cathode efficiency-current density curves according to Wesley and Roehl:¹⁸ A, hard bath; B, Watts pH 5.5; C, Watts pH 2.0; D, chloride bath.

pH.^{24,18} Typical cathode efficiency curves for nickel plating baths are given in Fig. 2, taken from Wesley and Roehl.¹⁸

Cathode potential curves are presented in Fig. 3, which shows that pH has no effect on the slope in the normal range, whereas rising chloride content has a somewhat beneficial effect, increasing the slope in the direction shown.¹⁸ No data are available on the effect of temperature and agitation on the slope of these Watts bath curves, although it is known that a rise in these factors reduces the polarization.

The preceding observations show that the throwing power of the Watts bath should be improved by an increase in pH, temperature, and nickel and chloride contents. Actual metal distribution tests^{24,25} confirm these effects in the low pH Watts bath but show that they are less

pronounced at high *pH*. At high current densities, the low *pH* Watts bath is only slightly inferior to other nickel baths in respect to throwing power and can be made superior by sufficient increase in its chloride content.¹⁸

Harr²⁴ noted that hydrogen peroxide reduced the throwing power of the low *pH* bath, but the effect did not last long after the addition had been made. He found that ferric sulfate is very detrimental to throwing power, but ferrous sulfate is not.

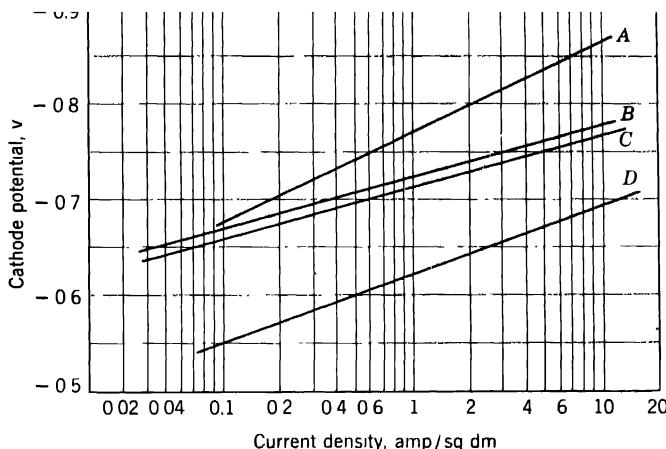


Fig. 3 Typical cathode potential-current density curves according to Wesley and Roehl:¹⁸ A, hard bath; B, Watts *pH* 5.5; C, Watts *pH* 2.0; D, chloride bath.

At least as important as throwing power in the determination of metal distribution of nickel deposits is the primary current distribution which, in turn, depends upon cathode shape. Pinner²⁶ discussed this factor and presented examples of improvement of plate distribution through improvement of methods of racking. Disregard of this factor can be the cause of waste of thousands of pounds of nickel through unwarranted overplating on certain areas in order to meet a minimum specification on others. Broadly speaking, each particular article to be nickel plated presents its own problem, and a careful study is recommended, the goal being as uniformly coated an article as the application of all pertinent knowledge can produce.

STRUCTURE AND MECHANICAL PROPERTIES OF DEPOSITS

Roehl,²⁷ Brenner, Zentner, and Jennings,²⁸ and Heussner, Balden, and Morse²⁸ report a wealth of data on the effects of *pH*, temperature, current density, and solution composition on the metallographic structure and mechanical properties of nickel deposits from the modern

Watts bath. These effects can be summarized in a general way as follows.

When plated at 55°C and pH 2.0, deposits from the modern Watts bath show a columnar or conical structure which grows coarser with increasing thickness. Grain refinement, or reduction in grain size, occurs as the pH is increased, the temperature decreased, or the chloride content increased. The effect of current density varies with conditions. The hardness, tensile strength, and ductility of nickel deposits are almost always consistently related; that is, an increase in hardness is accompanied by an increase in tensile strength and decrease in ductility.

Soft, ductile deposits are obtained at pH 4.5 or lower. For example, a tensile strength of 50,000 lb/sq in. (35 kg/sq mm), an elongation of 37% in 1 in., and a Vickers diamond pyramid hardness (10-kg load) of 100 were observed by Roehl²⁷ in nickel deposited at pH 4.5. As pH values were dropped below 3 the hardness rose slowly, but as the pH was increased above 5 the hardness rose rapidly, with a corresponding increase in tensile strength and reduction in ductility.

Current densities over the range 10 to 50 amp/sq ft had little effect upon the mechanical properties of the plate from the low pH bath, but at pH 5.0 there appeared to be some drop in hardness and tensile strength with increasing current density in this range. Brenner and Jennings²⁸ obtained a Knoop hardness (200-g load) of 175 in a bath at pH 3.0 and a low current density of 10 amp/sq ft. They found that the hardness reached a minimum of 135 at 40 amp/sq ft and then increased slowly with further rise in current density. An increase in temperature of the electrolyte had the expected effect of decreasing hardness and tensile strength and increasing ductility.

The increase in hardness and strength of nickel deposits made at high pH has been shown by Macnaughtan, Gardam, and Hammond²⁹ to be related to the amount of occluded basic compounds of nickel. These are believed to be codeposited in a finely divided or colloidal form dispersed through the nickel lattice in such a way as to interfere with slip. Brenner and Jennings²⁸ doubt that the relationship is as simple as that, since other factors, such as the structure and the cobalt content, play a role.

Nickel can be deposited with a wide variety of metallographic structures and with controlled physical and mechanical properties over a wide range of values. When other than a soft ductile nickel is required, bath compositions quite different from the Watts solution are employed. These are discussed later in this chapter.

THE BRIGHT NICKEL BATHS

The bright nickel solutions are basically Watts-type baths, containing nickel sulfate, nickel chloride, and boric acid to which have been added brighteners. The functions of the inorganic salts are the same as in the Watts-type bath and need little further discussion. However, conditions in the cathode film are more critical. They must be favorable not only for deposition of nickel but also for the functioning of the addition agents which modify the process. Therefore the nickel content is somewhat higher, 10 to 12 oz/gal, the chloride ion content should be at least 1.8 oz/gal and, in some solutions, as high as about 6 oz/gal, and the boric acid content should be not less than 5.0 oz/gal. Under these conditions, slight burning at extremely high current density points, which does no particular harm in dull nickel plating, is avoided. Also, the high boric acid content favors ductility and adhesion. Operating variables will be discussed below.

BRIGHTENERS OF THE FIRST CLASS

Many brighteners for nickel fall into two fairly distinct classes. The first class consists of those compounds which have in the molecules a $\text{--C}(\text{--})^{\frac{1}{+}}\text{SO}_3^-$ group. When added to the Watts bath, suitable compounds of this class produce bright plate on buffed surfaces. They also permit the use of higher concentrations of compounds of the second class and of reducible impurities.

The first class of compounds used in a Watts-type bath were the alkyl naphthalene sulfonic acids proposed by Lutz and Westbrook.³¹ More useful have been the unsubstituted aryl polysulfonates with from two to three sulfonic acid groups (Schlötter¹²), especially the naphthalene disulfonic acids, of which the 1,5-acid is specifically preferred by Waite.³² α - and β -Naphthalene monosulfonic acids, α -naphthylamine-3,6,8-trisulfonic acid, three toluidine sulfonic acids, and *o*-toluidine disulfonic acid have also been mentioned.^{32, 33} Harshaw and Long³⁴ suggest diphenyl sulfonates, and Kosmin³⁵ diphenylbenzene and hydrogenated diphenylbenzene polysulfonates.

In all these sulfonic acids the double-bonded carbon is furnished by the aryl ring. However, Hoffman³⁶ cites a number of substituted ethylene and aldehyde sulfonic acids, said to be especially suitable in high chloride baths, in which the double bond, in α -position to the sulfonic group, is furnished by the alkylenic chain or aldehyde group. Accord-

ing to him, the double bond may also be in β -position to the sulfonic group and have the general formula =C—C—SO—.

Brown^{37 40} has added several subclasses to the general class =C—SO—. These brighteners include the very important aryl sulfonamides and sulfimides,³⁷ a preferred combination in his baths being *p*-toluene sulfonamide and *o*-benzoyl sulfimide. They provide nickel baths with a lesser sensitivity than the sulfonic acids to brighteners of the second class and to reducible impurities.

In his discussion of this class of compounds, Brown points out that the strength of the C—S bond is important and is modified by other active groups present. With the less soluble compounds, brightening is manifested mainly in low current density areas. As in the sulfonic acids, the double-bonded carbon of the sulfonamides can be supplied by α - or β -unsaturated aliphatic groups.³⁸ The α -compounds are somewhat more effective in increasing tolerance to brighteners of the second class and to reducible impurities. Their own brightening effect, on the other hand, is less pronounced than that of the β -compounds. The main value of the unsaturated aliphatic sulfonamides is in high chloride, nickel baths.

Another subclass disclosed by Brown is the arylsulfinic acids,³⁹ such as the benzene- and the *p*-toluene sulfinic acids, which are more effective than the aryl sulfonic acids and sulfonamides in increasing tolerance to many substances which by themselves give peeled or dark plates or misplating in low current density areas. In this patent

Brown continues his discussion of structure of =C—SO— compounds.

The last subclass proposed by Brown consists of arylsulfone sulfonates⁴⁰ in which the arylsulfone group provides superior brightness and greater tolerance to zinc and organic substances than the aryl group.

BRIGHTENERS OF THE SECOND CLASS

The second class of brighteners, used in all modern bright nickel baths, differs from the first class in that its members cannot be used alone in a Watts-type or high chloride bath without producing excessive brittleness and stress in the nickel deposits. The color of the deposit also leaves much to be desired even when optimum amounts are added. They become important only when used in conjunction with brighteners of the first class, which reduce brittleness and stress. Suit-

able combinations of brighteners of the two classes furnish the highly mirror-like luster required in modern bright nickel plating.

Like the brighteners of the first class, those of the second contain several subclasses. In fact, the subclasses differ very greatly from each other chemically.

The first of these subclasses comprises ions of metals which are characterized by high hydrogen overvoltage in acid solutions. They include ions of zinc,^{32, 33, 36-38, 41} cadmium,^{32, 33, 36, 38, 41} and mercury^{38, 42} in the second subgroup of Group II of the periodic system, and thallous^{38, 39} and lead⁴³ ions, which metals are found side by side with mercury in the third long period of the periodic system. Lead, which is nearly insoluble in the Watts bath, was introduced with large additions of citric acid, and apparently was present at supersaturation, easily disturbed. One metal with high hydrogen overvoltage, tin, is not included in this list, but Viers and Case⁴⁴ cite it with zinc, cadmium, and lead as furnishing ions that cause grain refinement of nickel deposits.

To this first subclass of the second class may also belong certain compounds of sulfur,⁴⁵ selenium,^{34, 46} tellurium,³⁴ and arsenic.⁴⁷ The first three of these elements belong to the second subgroup of Group VI of the periodic table, and arsenic to the second subgroup of Group V. All of them (as well as mercury, antimony, and bismuth) are known to make iron absorb hydrogen during pickling, either by increasing the hydrogen overvoltage or by a poisoning effect which reduces the ability of iron to catalyze the reaction $2H \rightarrow H_2$.⁴⁸

The second subclass of the second class of nickel brighteners comprises organic compounds containing unsaturated C=O, C=C, C≡C, C=N, N=N, and N=O groups. The presence of these groups, however, does not guarantee that the compound is a good brightener, because other bondings and groups in the molecule may seriously interfere with their effects.

The prototype of the C=O compounds is carbon monoxide, which in fact produces bright, cracked deposits.⁴⁹ In monoketones^{50, 51} the C=O group has hardly any effect, but in the polyketones it does. The aldehydes are still more effective, especially formaldhyde^{52, 53, 42} and the chlor- or brom-substituted aldehydes.⁵¹ The effects of structure of aldehydes is discussed by Brown.^{50, 51}

As a rule, carboxylic acids have no brightening effect. An exception is formic acid.^{52, 53, 42}

The most active aldehydes are those which contain a C=C group in addition to the C=O group.^{50, 51, 54} The practical usefulness of these aliphatic aldehydes, however, is slight because of their great tendency to form resins which interfere with the nickel deposition ("skipping").

The aryl aldehydes are slightly soluble in the nickel bath and are, by themselves, valueless. However, the sulfonated aryl aldehydes^{45, 55, 56} have seen considerable commercial application, especially *o*-sulfobenzaldehyde.^{45, 55} It is possible that the slight unsaturation characteristics of the aryl ring strengthens the unsaturation characteristics of the aldehyde group. Freed and Stocker⁴⁵ comment that the benzene derivatives are more desirable than the naphthalene and the anthracene derivatives. Sulfoacinnamaldehyde, having a C=C group in α -position to the C=O group, shows a particularly strong brightening effect.

The sulfonated aldehydes combine in one molecule both the C=O and the $=C-\overset{+}{SO}_-$ groups and hence can be used alone in the nickel bath without further addition of sulfonates, etc. However, the preferred sulfonated aldehydes seem to perform better when other desirable sulfonates are also present.^{45, 55}

Similar combinations of the $=C-\overset{+}{SO}_-$ group and unsaturated groups are offered by the substituted ethylene sulfonic acids of Hoffman³⁶ and by the ethylene sulfonamides and the chlor- and brom-substituted ethylene sulfonamides of Brown³⁸ already discussed in connection with the first class of brighteners. Brighter plate may be

had when there is also present a regular $=C-\overset{+}{SO}_-$ compound or a metallic ion brightener.^{36, 38} The tolerance to the latter ions and to copper³⁸ contamination is raised most effectively by these aliphatic $=C-\overset{+}{SO}_-$ compounds. Brown³⁸ points out that his compounds,

like all $=C-\overset{+}{SO}_-$ compounds, can be used in any desired concentration up to saturation. What has been said about these ethylene derivatives also holds true of the previously discussed β double-bond compounds in the same patents.^{36, 38}

A number of other compounds containing the C=C bond and requiring the presence of compounds of the first class have been mentioned in the patents. They include allyl compounds³⁸ and certain alkaloids;⁵⁷ the complex structure of the latter, however, makes their value questionable. The C≡C bond occurs in acetylene, which has a brightening effect when bubbled through a Watts-type nickel solution.

A large number of brighteners containing the C=N group have been proposed. Among them are the important safranines and other

azines,⁵⁷⁻⁵⁹ oxazines^{57, 59} and thiazines,^{57, 59} indamine and indophenol dyes,^{57, 60} and the di- and triphenyl amine derivatives,^{57, 61} of which decolorized fuchsin is the preferred example. Most of the compounds are employed in very low concentration, of the order of 0.3 to 13 oz/1000 gal, and produce extreme brittleness when used alone; some also produce streakiness and burning. The most effective compounds of the first class are needed to reduce brittleness and other defects.

No compounds carrying C≡N have been encountered in the literature on bright nickel.

Lind and co-workers have also patented the use of compounds carrying the N=N group, namely the azo dyes and other azo compounds.^{58, 63} They indicate some of the limitations on structure and substituent groups; these are similar to those given for the C≡N compounds.

Brown⁵⁴ has suggested compounds containing N=O groups. Those that in addition carry a C=C group in α -position are more effective than the saturated nitro compounds (paralleling the difference between crotonaldehyde and butyraldehyde). Sulfonic derivatives, such as the 2-nitrovinyl benzene sulfonic acids, are preferred, because the sulfonic group eliminates the low solubility and oiliness that otherwise are encountered. They are said to give very bright, ductile plate.

UNCLASSIFIED BRIGHENERS

The baths developed by Weisberg and Stoddard,^{52, 53} Hinrichsen,⁴² and Freed⁴¹ contain added cobalt. An excess seems to have no detrimental effect on brightness. Cobalt improves the corrosion resistance of the deposit. The cobalt content usually falls within the range of 1 to 20% of the deposit. The formate ion^{52, 53, 42} can also be used in high concentration.

Weisberg and Stoddard^{52, 53} have used a small amount of ammonium ion to produce brightness, but an excess causes darkening and embrittling of the deposit. Its use is unnecessary in solutions purified according to modern standards.⁶² Simple amines have a brightening effect, but the accompanying darkening and embrittlement of the

deposit is not overcome by the use of C=S—O— compounds in high concentration. The brightening produced by certain useful compounds of the second class containing amino groups^{57, 59-61, 63} therefore appears to be due largely to the unsaturated bonds and not to the amino group or groups.

BRIGHTENER REACTIONS AT THE CATHODE

Brown³⁹ visualizes the primary cathode reactions as reductions. Nickel is believed to catalyze the reduction of compounds of the first class. The sulfur-containing reduction products of the brighteners of class two are thought to poison the catalytic nickel and thereby regulate the reduction of brighteners of class one as well as of reducible impurities. This view is supported by analysis of deposits for carbon and sulfur and by Brown's demonstration⁴⁴ of the catalytic effect of nickel and its poisoning.

The actual mechanism of brightening is not understood, although several attempts have been made to explain it.⁴⁵⁻⁴⁹

CHOICE OF BRIGHTENERS

A consideration of the chemical reactions indicates that the particular configuration of the molecule carrying the brightener group and the nature and exact position of substituent groups in the molecule should be of considerable importance in at least three respects. The many comments in the patents support this view. First, these factors determine the solubility of the compound, which must be high enough to supply a sufficient amount of brightener without oily effects. Second, the substituent groups must not be such that they or their reduction or reaction products exert an unfavorable effect on the plate. Such an effect may be offset substantially by insufficient concentration of such groups or reaction products, by their position in the molecule, or by the presence of suitably positioned other groups which neutralize their effect. Third, the substituent group must not lessen the reactivity of the brightener group too much, particularly that of a relatively weak brightener group, and it may be desirable to increase it. However, if increased reactivity causes resinification in the body of the solution, it becomes undesirable.

Bath composition and operating factors will influence the rate and possibly the mode of reduction of the brighteners. This is particularly true of the compounds of the second class, which as a rule are the more critical; those of the first class function well within wide ranges as long as they are added in sufficient quantities and are sufficiently soluble. Many compounds of the second class do not function well in high chloride solutions. Some give bright plate (in the presence of compounds of the first class) only within limited current density ranges. All function best within a particular, frequently

narrow, *pH* range which varies with the type of compound and even with its individual structure.

Practicably, only a limited number of compounds are of commercial value in producing bright deposits. When one considers that there are other factors than brightness, the choice becomes even narrower. The corrosion resistance provided by the deposit must not be lowered, and hence conditions producing desired brightness must not facilitate codeposition of harmful impurities (copper, for example, is very harmful⁷⁰) or result in deposits having both high stress and low ductility. According to Lyons,⁷¹ many effective brighteners are not acceptable because they materially reduce adhesion by becoming adsorbed on the basis metal surface. Brown⁷¹ has shown that furfural, which is an active brightener of the second class, in an amount of about 0.134 oz/gal causes the nickel deposit to adhere poorly to steel but does not interfere with the adhesion to a cyanide copper flash deposit. Whether this is a question of adsorption of the brightener itself or of the difference in reducibility at the different cathodes and subsequent adsorption of the reduction product itself or of condensation products was not determined. Brightness is not always accompanied by desirable smoothing action; in fact, semi-bright deposits may be smoother than bright deposits.^{72,73}

WETTING AGENTS

Because hydrogen peroxide oxidizes unsaturated organic brighteners (formaldehyde is oxidized to desirable formic acid, which is not oxidized further), it cannot be used to prevent pitting in bright nickel baths containing such brighteners, if for no other reason than that of cost. Bright nickel baths containing certain aldehydes^{52,53,54,55,56} are seldom subject to pitting and may not require special anti-pitting agents. In other baths, wetting agents are used to reduce the contact angle between bubbles of hydrogen or other gases, such as air, and the nickel surface and make the bubbles disengage themselves before they can reach pitting size.

Sulfates of normal primary alcohols containing from 8 to 18 carbon atoms, especially the sodium lauryl sulfate,⁷⁴ were the first wetting agents used and are still employed to a large extent. Alkyl-substituted benzene sulfonates with from 10 to 19 carbon atoms in the alkyl chain⁷⁵ have also been used. Lately, other types of compounds have been suggested for this purpose, examples of the different types being sodium lauryl sulfoacetate,⁷⁶ sodium monolaurin monosulfate,⁷⁷

the sodium salt of lauric acid monoester of diethylene glycol sulfo-acetate,⁷⁸ and 1-oxydodecyl-1-sodium sulfonate methane.⁷⁹

Except for the alkyl benzene sulfonates, compounds with a straight chain are preferred to those with branched chains. The most satisfactory chains usually contain from 12 to 14 carbon atoms. The concentration of these compounds varies with type and kind but is usually of the order of 0.067 oz/gal. With a high content of oil or grease in the bath, higher-than-normal concentrations of wetting agent are sometimes used, but such practice is likely to cause difficulty with the corrosion resistance of the nickel deposit. Because of their high surface activity, wetting agents tend to adhere to the nickel surface, and their loss by drag-out is higher than that of any other constituent of the bath. Care must be taken that adhering wetting agent is removed by thorough rinsing prior to chromium plating. The rinse may be followed by a short cathodic cleaning operation, a second rinse, acid dipping, and a third rinse.

Because all bright nickel processes are proprietary and subject to change, the present authors find themselves unable to discuss the individual baths. They suggest that the recommendations of the purveyors of bright nickel solutions be followed.

SEMI-BRIGHT NICKEL PLATING

Because of inherent brittleness, bright plates from solutions containing organic addition agents have been restricted in application. Such limitation is important where parts are subjected to externally applied stress as, for example, are automobile bumper bars. A further limiting factor is the inability of bright plate to hide or cover up such imperfections in the basis metal as deep polishing scratches.

Deposits from the Watts bath have been used where bright nickel was not applicable, but they have the disadvantage of requiring a comparatively large amount of buffing in order to provide the desired luster. Thus industry has had to choose between: (1) a rather soft, draggy Watts plate having excellent ductility, and (2) a hard, brittle, bright plate possessing practically no flowing properties under the buffing wheel for scratch-hiding.

Recently, nickel plate has become available which is intermediate in hardness, ductility, and grain size between the Watts-type plate and the bright plate. These deposits have been designated semi-bright and have filled the requirement of a nickel coating possessing excellent buffing properties together with acceptable ductility and good scratch-hiding properties. There are two classes of baths for such deposits. Both have the basic Watts bath formula: one^{72,73}

employs organic addition agents, and the other is a modification of the bath producing the bright cobalt-nickel alloy.⁶²

The semi-bright plate allows a marked reduction in the cost of buffing labor and materials. In addition, the smaller amount of metal removed lowers the nickel plating cost because less plate is required before buffing in order to arrive at the required thickness afterwards. As a substitute for bright nickel in certain applications, the semi-bright nickel makes possible savings in basis metal polishing costs. Inasmuch as the plate has good scratch-covering power, plus good flowing ability under the buffing wheel, the quality of the basis metal polish may be lower. As far as the basis metal composition is concerned, the semi-bright nickel plating baths are used in the same manner as the Watts or bright plating solutions.

SPECIAL PURPOSE BATHS

A number of applications for nickel plate require baths of special composition. Those to be considered now are operated at low bath temperatures, to avoid deleterious effects upon the basis material. Bath formulas and preferred operating conditions are shown in Table 2.

ELECTROTYPEING BATHS

Solution A of Table 2 is typical of those recommended for plating over wax and lead molds.⁸⁰ The ammonium salt increases conductivity and provides buffer action at the high pH. Boric acid is not included because it leads to undesirable stress and cracking of the plate at such low temperature, high pH conditions which are necessary for covering or spreading over the surface of a treated wax mold. Air agitation is commonly employed to permit operation at the upper end of the current density range. In plating on stereotypes, where the problem of covering is not serious, some modern electrotypers apply nickel from standard hot baths or from bath J at current densities as high as 40 to 50 amp/sq ft.

THE DOUBLE SALT BATH

Solution B finds little application in this country, although it is representative of still baths widely used abroad. It can be employed only at room temperatures and low current densities. It is used for deposition of thin coatings, e.g., on brass, cheap jewelry, and novelties: A former, common practice was to add a brightener like gum

TABLE 2. SPECIAL PURPOSE NICKEL BATHS

Solution	Ingredients	Concentration		pH (electro- metric)	Temperature		Normal Cathode Current Density,* amp/sq ft
		oz/gal	g/l		°F	°C	
A. Electrotyping	Nickel sulfate	9	70	5.6-6.0	90	32	10-20
	Ammonium chloride	0.7	6				
B. Double salt	Nickel sulfate	16	120	5.0-5.5	room	room	5-10
	Ammonium chloride	2	15				
	Boric acid	2	15				
C. Barrel plating	Nickel sulfate	20	150	5.0-5.5	75-90	24-32	.
	Ammonium chloride	4	30				
	Boric acid	4	30				
D. High sulfate	Nickel sulfate	13	100	5.3-5.8	70-90	21-32	10-35
	Ammonium chloride	4	30				
	Anhydrous sodium sulfate	13	100				
	Boric acid	2	15				
E. Black nickel	Nickel sulfate	10	75	5.6-5.9	120-130	49-54	5-20
	Nickel ammonium sulfate	6	45				
	Zinc sulfate	5	37				
	Sodium thiocyanate	2	15				
F. Hard nickel	Nickel sulfate	24	180	5.6-5.9	110-140	43-60	25-50
	Ammonium chloride	3.3	25				
	Boric acid	4	30				
G. Chloride	Nickel chloride	40	300	1.5-2.0	140	60	25-200
	Boric acid	4	30				
H. Chloride-sulfate	Nickel sulfate	26	200	1.5-2.0	115	46	25-100
	Nickel chloride	23	175				
	Boric acid	5.3	40				
J. Chloride-acetate	Nickel chloride	17.2	130	4.5	120	49	50
	Nickel acetate	18	135				

* Cathode current density permissible in still baths or with agitation only sufficient to prevent stratification. Higher current densities are possible with increased rate of agitation.

tragacanth, gum arabic, or cadmium salts, but these deposits were very brittle and were apt to fail when chromium plated.

BARREL PLATING BATHS

Solution C, being more concentrated than B, has the wider range necessary for the barrel plating of small parts in bulk. The brighteners used with bath B are also encountered here. Modern proprietary bright nickel baths are now available for barrel plating to yield a superior product at higher rates of plating.^{81,82}

THE HIGH SULFATE BATH

Solution D is of a type developed by Thompson⁸³ for plating nickel directly upon zinc alloys. The high content of sodium sulfate sup-

presses ionization of the nickel sulfate and thus prevents deposition of granular nickel by chemical displacement on the zinc surface. Because the nickel deposits from this bath are brittle and highly stressed, a thickness limitation of less than 0.001 in. (0.025 mm) is imposed. This necessitates transfer of the plated part to a second nickel bath, and difficulties encountered in securing good adhesion between the two nickel layers have caused solution D to be supplanted by the cyanide copper bath.⁸⁴ It is described here because it has a high throwing power and may be useful in plating on aluminum and magnesium alloys which have been coated with zinc by an immersion process.

THE BLACK NICKEL BATH

Bath E is special for deposition of a decorative black finish which contains not only nickel but also large amounts of zinc and sulfur. Details can be found in an article by Poor.⁸⁵ For better corrosion protection, a layer of pure nickel can be deposited on the basis metal prior to black nickel plating.

MAINTENANCE AND CONTROL OF NICKEL BATHS

A modern nickel plating bath may be regarded as a highly complicated piece of production equipment and should therefore be accorded all the attention that is given to any piece of precision machinery. Oversight or neglect of any phase of maintenance or control of the nickel plating process can lead only to defective work, lost time, and high production cost.

Maintenance and control should start with the installation of the tank and its auxiliary equipment. Satisfactory, thoroughly tested tank linings and internal heating elements are available and are generally used. Heating of the solution by means of an external heat exchanger is much to be preferred. Of the materials used for internal heating elements, lead, carbate, and glass coils are commonly employed. Whereas lead was at one time used almost exclusively, it has in later years been replaced by either carbate or glass in order to avoid the possibility of metallic contamination. Lead is soluble in high chloride nickel baths. For this reason lead coils should not be used where the nickel chloride content is higher than 8 oz/gal.

Carbate heating elements are widely used in such baths, and, since they have very excellent heat transfer properties, they may be employed in any type of nickel plating solution. The one disadvantage of such heating elements is their fragile nature, which requires unusual pre-

caution to place them in such a position in the tank that physical damage becomes unlikely. Glass heating coils avoid both metallic contamination and stray electrical currents, but have the disadvantage of a relatively poor coefficient of heat transfer.

Since insulation defects may be the direct cause of poor adhesion and may result in current loss or poor plate distribution, tanks should be mounted on positive insulators such as glass or glazed ceramics. All piping connections for water, steam, and air exhaust should be equipped with permanent insulating joints in order to avoid electrical grounds and short circuits. The ground lights, described by Borchert and Kinnaman,⁸⁶ are useful control devices. The use of wood for drip boards or anode-rod supports is objectionable. All anode and cathode bars, racks, and contact points should be kept reasonably free from encrusted salts in order that good electrical contact be maintained. Contamination of the bath with copper must be avoided. Wrapping the anode bars with polythene sheeting is a step in that direction.⁸⁷

The best maintenance and control is effected by providing adequate facilities for proper cleaning and preparation of the work. Complete removal of grease, solid particle dirt, oxide, scale, and smut is necessary if adherent, relatively non-porous and smooth deposits are to be secured. Sufficient rinsing facilities, preferably in the form of small multiple-compartmented tanks,⁸⁸ must be provided to obviate carry-over of soaps, solid particle dirt, and metallic salts of copper, iron, or zinc into the nickel solution.

Conveyors or other mechanisms over the plating tanks must be provided with drip pans or shields to prevent bath contamination by oil and grease. The plating line should be located in a plant area which is blocked off from contamination by air-borne dusts. Metal dusts are particularly objectionable. For this reason there should be no direct openings to the grinding, polishing, or buffing departments, or else the plating department should be completely enclosed and under higher air pressure than the other departments.

Where production is fairly well standardized and tank loads are fairly constant, a balance between anode and cathode area can usually be reached for the particular bath composition, etc. The metal content of the bath will remain fairly constant, and additions of nickel salts will be required only periodically when batch filtrations are made. Analysis for all bath components is necessary at proper frequency if maximum operating efficiency is to be maintained. Concentrations of brighteners and other addition agents often require accurate control.

EFFECT OF CONTAMINANTS

In the modern nickel plating bath, minute quantities of metallic contaminants such as iron, zinc, copper, or lead exert a profound effect on the appearance, corrosion resistance, and buffability of the deposit. There is evidence that impurities in combination may exert effects that are different from what might be expected from the effects of the individual impurities. Madsen⁸⁹ noted that increasing amounts of codeposited iron increased the brittleness of the nickel plate from a high pH bath. Pinner has noted that even a small quantity of iron profoundly affects the buffability and corrosion resistance of semi-bright nickel deposits. Low pH baths tolerate larger quantities of ferrous ion.

Copper in excessive amount causes dark-colored, hard-to-buff deposits. It is also detrimental to bright nickel deposits, especially in low current density areas. Phillips⁹⁰ observed that copper may be the cause of nickel pitting in a low pH Watts bath; Ewing and Gordon⁷⁰ found that it seriously affected the corrosion resistance of nickel deposits. Generally, zinc in sufficient quantity has much the same effect as copper in a nickel bath. Haring⁹¹ noted that both copper and zinc exert a deleterious effect on throwing power, particularly at low current densities; Anderson⁹² reported that excess zinc causes cracking and poor resistance to corrosion. Lead causes peeled, fine-grained, and brittle deposits.

For further details about the effects of these and other impurities, see the literature review by Ewing and Gordon.⁹³ The amount of metallic impurities which can be tolerated in a nickel plating bath depends on several factors. One set concerns the concentrations of main bath constituents. Bright and semi-bright nickel baths are often more susceptible than plain Watts-type solutions, and they differ greatly in respect to individual impurities. Since metallic contaminants tend to plate out in the low current density areas, the amount which can be tolerated will depend in part on the shape of the cathodes. Since they affect corrosion resistance and ductility of the deposit, the service which will be required is another factor.

REMOVAL OF METALLIC CONTAMINANTS

Most metallic contaminants can be removed fairly successfully by precipitating as an insoluble salt and then filtering. In plants processing steel, iron is usually the principal contaminant. It may be re-

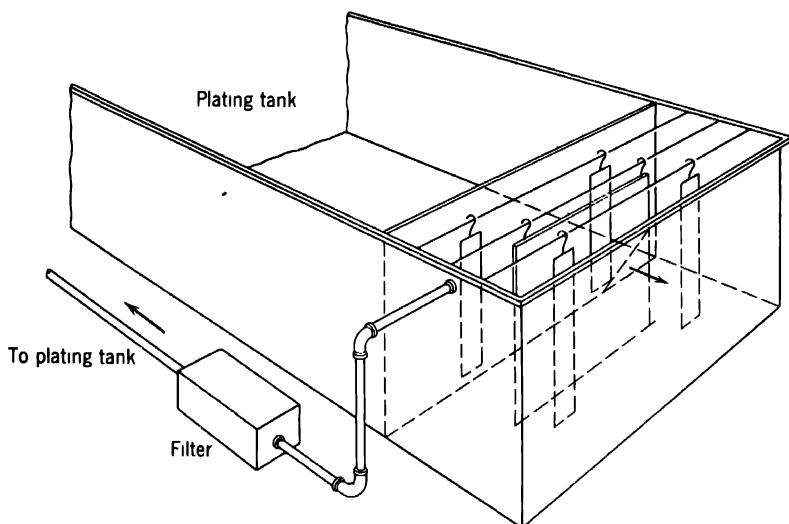


Fig. 4. Schematic view of electrolytic purification unit built into plating tank, according to Case.⁹⁵ A rubber suction hose attached to filter can be used to pick up heavy dirt from bottom.

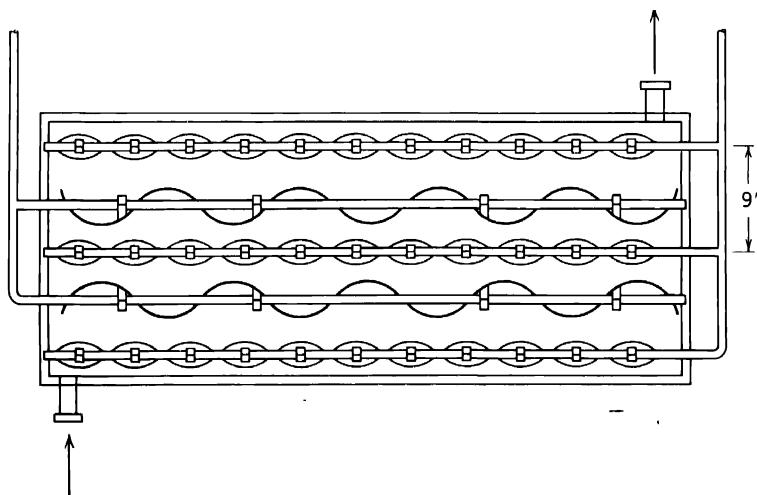


Fig. 5. Schematic top view of separate tank for electrolytic purification, according to Case.⁹⁵ Inlet and outlet are on different levels, bottom of tank or solution level. Note corrugation (actually about 1½ in. deep, 2 in. apart) to give sufficient variation in current density for simultaneous removal of different impurities.

moved by adding, with agitation, nickel carbonate or nickel hydroxide in water suspension until the pH reaches a value of 5.5. If the character of the bath permits oxidation to the ferric state, precipitation will occur at a pH as low as 4.0. Aluminum hydroxide is also precipitated at a pH of 4.0. At a pH of 5.5, zinc hydroxide precipitates. Care should be exercised when raising the pH of a nickel bath with hydrated lime not to exceed a pH of 6.5, since nickel hydroxide may be precipitated and lost in the filter cake. Also, any carbon dioxide evolved from use of nickel carbonate must be removed by heating, or brittleness of the plate will result.⁴⁹

In plants processing copper, brass, or zinc-base die castings, the principal contaminants are likely to be copper and zinc; if not present in too great quantities, these impurities usually plate out of the bath by deposition in the low current density areas of the work. Copper, if present in considerable quantities, however, may be removed by electrolytic displacement on iron or nickel powder, following which the bath must be treated to raise the pH to the point where iron will be precipitated and filtered. Complete removal of metallic contaminants is quite unlikely to take place when precipitation methods are employed. Although fairly effective, they are expensive, because the bath must be completely out of operation for an appreciable period of time.

Modern practice calls for removal of metallic contaminants by low current density purification as recommended by Weisberg.⁵⁴ Such treatment is preferably continuous. Case⁵⁵ and others have laid out complete and detailed procedures. By the proper choice of current density and cathode shape, iron, zinc, copper, and lead may all be removed during the same period of electrolysis. Pinner has observed that low current-density purification of baths containing organic addition agents, even in the absence of metallic contaminants, is sometimes effective in improving salt spray corrosion results. Figures 4 and 5 show two arrangements for electrolytic purification recommended by Case.⁵⁵

REMOVAL OF ORGANIC CONTAMINANTS

Organic contaminants cannot be removed by conventional filtering procedures. They may result from air-borne dusts, inferior cleaning methods, breakdown of organic addition agents during the normal course of operation, or improperly chosen tank linings or rack coatings. They are effectively dispersed by wetting agents and cause

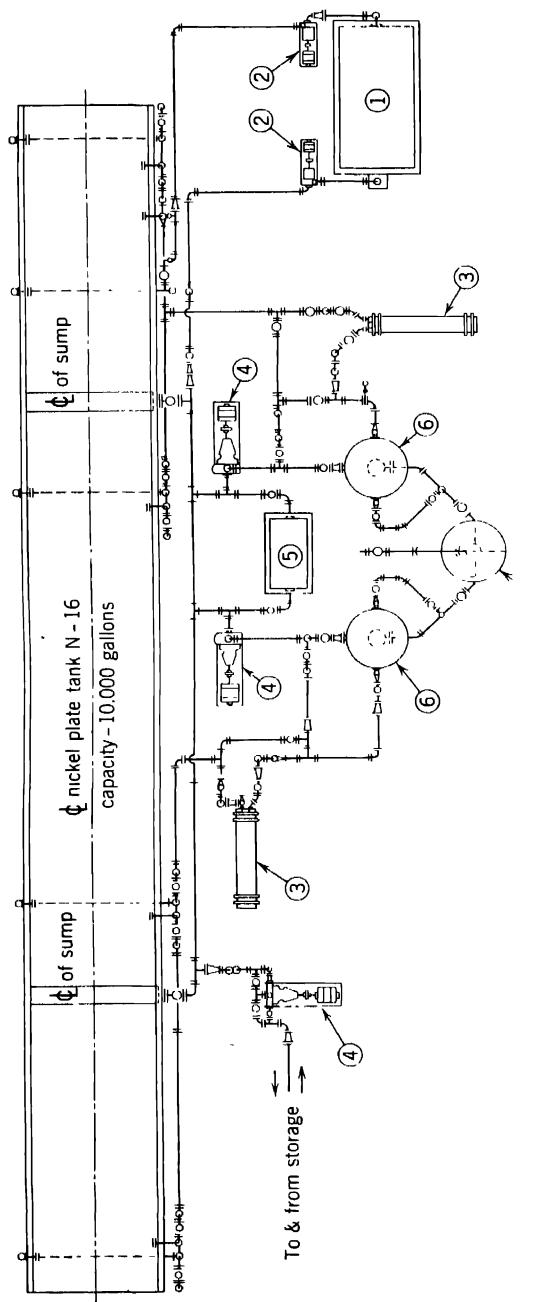


Fig. 6. Schematic drawing of modern filtration and purification system, according to Cole: (1) tank for continuous electrolytic purification, (2) pumps for same, (3) heat exchangers, (4) pumps, (5) tank for making salt additions to solution or slurry for filters, (6) filter, (7) filter clean-out tank

various difficulties. Oil and grease, for example, cause the so-called grease pitting.

This type of contaminant is best controlled by adsorption on activated carbon. In this treatment the solution is pumped to an auxiliary tank where it is mixed with 1 to 2 lb/100 gal of activated carbon, raised to a temperature of approximately 65°C, and allowed to digest while being stirred for a period of several hours. Before the temperature is raised, it is often advantageous to add an oxidizing agent such as hydrogen peroxide in sufficient quantity to convert any non-oxidized organic matter present. Filtration (with filter aid) results in a clean solution which is reasonably free of most organic contaminants. If the pH of the bath is raised during the period of carbon treatment, some of the metallic contaminants are also effectively removed.

During the normal course of operation, solid particle dirt is constantly introduced. This dirt owes its origin to anode sludge, airborne dust particles, welding scale on work pieces, or one of many other sources. It must be constantly and efficiently removed; otherwise rough or pitted deposits will occur.

Plating solution filters are of many types, most of which are effective. It is general practice to lay a filter cake of activated clay, finely divided asbestos, or diatomaceous earth over the filtering surface, whether it be a cloth, filter paper, or ceramic material, before filtration is begun. These coatings support the dirt and help in maintaining the porosity of the filter surface which would otherwise quickly become clogged. The rate of filtration is usually dictated by the amount and kind of work processed through the tank. For steady, heavy duty operation it has been found advisable to use a rate of filtration such that the entire solution passes through the filter within a period of 1 to 2 hr.

Figure 6 shows a modern filtration and purification system described by Cole.⁹⁶

DETERMINATION OF MAIN BATH CONSTITUENTS

CONTROL OF pH

pH is measured by colorimeter tubes or pH papers, or by quinhydrone or glass electrodes. The true electrometric pH is about 0.5 pH less than the apparent value obtained colorimetrically. Throughout this discussion all pH values cited are electrometric unless specifically stated otherwise.

Knowledge of the allowable range of pH for the particular bath, and of its rate of change, should govern the frequency with which pH

determinations and corrections are made. For the Watts or bright nickel plating baths, the *pH* will ordinarily be found to increase during use; it is lowered by the addition of sulfuric or hydrochloric acid or both. The choice depends on which anion is needed. So-called plastic nickel hydrate (which has not been allowed to dry after precipitation) is preferred for raising the *pH* because the carbon dioxide produced with nickel carbonate is likely to cause embrittlement of the deposit. The addition of any of these materials must be followed by filtration to prevent roughness.

DETERMINATION OF SURFACE TENSION

The determination of surface tension and the maintenance of the correct concentration of wetting agents are based on measurements with a tensiometer or with a stalaginometer, which is less sensitive to the effect of impurities. These pieces of equipment and their use are fully described in the journal literature⁹⁷ and in textbooks, to which the interested reader should refer.

ANALYTICAL METHODS

The following approximate methods of analysis are entirely satisfactory for commercial plating plant operation. The value of an analysis is proportional to the care with which the sampling of the solution is carried out. In obtaining samples for analysis, usual precautions should be taken, including bringing the bath to normal operating level so that the samples will be as truly representative of the whole bath as possible. Since stirring of the nickel bath is usually not advisable, a convenient method is to take samples with a glass or rubber tube having a length equal to the depth of the tank. By lowering the tube gradually until its lower end touches the bottom and then closing its top, a solution sample representative of solution at all depths in the tank is obtained. Several such samples should be taken at different locations and mixed to give the final sample.

Determination of Total Nickel. A 5-ml sample of the nickel solution is pipetted into a 250-ml Erlenmeyer flask and diluted with about 50 ml of water. Then are added, in order: a few drops of 10% potassium iodide solution, concentrated ammonium hydroxide until the color of the solution just turns a clear blue, and a few drops of 0.1 *N* silver nitrate solution. The resulting solution is titrated with 0.5 *N* sodium cyanide solution to a clear amber endpoint. Since the cyanide solution is very unstable, it must be frequently standardized against a known nickel solution.

To compute the nickel content, the milliliters of 0.5 *N* silver nitrate solution are subtracted from the total milliliters of 0.5 *N* sodium cyanide solution used. This value is used in the following formula:

$$\text{Normality of total nickel} = \frac{(\text{ml NaCN solution}) \times 0.5}{5}$$

A 1.0 *N* solution contains 29.34 g/l of metallic nickel, equivalent to 134 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 140 g/l $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, or 118 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.

Determination of Chloride. A 5-ml sample of the nickel solution is pipetted into a 250-ml Erlenmeyer flask and diluted with about 50 ml of water. A few drops of 5% potassium chromate solution are added. The solution is titrated with 0.1 *N* silver nitrate solution until the precipitate formed is tinged with a red color. The milliliters of silver nitrate solution used are noted and employed as in the following formula:

$$\text{Normality of chloride} = \frac{(\text{ml AgNO}_3 \text{ solution}) \times 0.1}{-}$$

A 1.0 *N* solution of chloride contains 35.4 g/l of chloride ion, equivalent to 118 g/l of nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, or about 80.5 ml/l (10.2 fl oz/gal) of hydrochloric acid (sp. gr. 1.19).

Determination of Boric Acid. A 2-ml sample of the nickel plating solution is pipetted into a 250-ml Erlenmeyer flask. No water is added. Then are added, in order: a few drops of indicator solution composed of 0.2% brom-thymol blue and 1% brom-cresol purple in 93% ethyl alcohol; ⁶⁸ from a burette enough 0.5 *N* sodium hydroxide solution until the color just changes from green to blue; and sufficient powdered mannite to make a thick paste, which makes the color turn green again. The mixture is then titrated with 0.5 *N* sodium hydroxide solution to a blue endpoint. The volume of sodium hydroxide solution used after the mannite addition is read from the burette. The 0.5 *N* NaOH solution should be standardized against a nickel solution containing a known amount of boric acid, normal for the type of bath being analyzed. The factor thus obtained is used in the analysis.

Determination of Sodium Sulfate in a High Sulfate Bath. A 10-ml sample of plating bath is diluted to 100 ml in a volumetric flask and a 5-ml aliquot is transferred to an Erlenmeyer flask. To this sample are added 7 ml of concentrated hydrochloric acid (sp. gr. 1.18) and 150 ml of water. The solution is brought to a boil, and 25 ml of 5% barium chloride solution are added with stirring. After standing for 1 hr, the solution is filtered through a weighed Gooch crucible and the

barium sulfate precipitate washed several times, first with 1% hydrochloric acid (by volume, concentrated acid, sp. gr. 1.18), then with distilled water. The crucible is heated to a red heat for 15 min, cooled in a desiccator, and reweighed.

The sodium sulfate content is calculated as follows:

Normality of $\text{Na}_2\text{SO}_4 = 17.14 \times$ grams barium sulfate — (normality of total nickel content — normality of chloride content); oz/gal $\text{Na}_2\text{SO}_4 = 9.5 \times$ normality of Na_2SO_4 ; g/l $\text{Na}_2\text{SO}_4 = 71 \times$ normality of Na_2SO_4 .

Determination of Hydrogen Peroxide. One hundred milliliters of the nickel plating solution is pipetted into a 300-ml Erlenmeyer flask, and a rapid stream of carbon dioxide is bubbled through it for 4 min. After 2 min, 5 ml of each of a standard starch solution and a 10% potassium iodide solution are added. At the end of 4 min, the carbon dioxide is stopped and the solution is titrated rapidly with 0.01 N sodium thiosulfate solution (standardized daily against potassium acid iodate) until the blue color disappears. One milliliter of 0.01 N sodium thiosulfate solution = 0.0017 g/l hydrogen peroxide = 21.5 ml 30% hydrogen peroxide/1000 gal.

Estimation of Metallic Impurities. Of the many methods used in the analysis of metallic impurities, the simplest are usually the colorimetric. Suitable methods for lead, iron, manganese, copper, silica, sodium, potassium, cadmium, aluminum, ammonium, chromium, zinc, and calcium have been developed or standardized by Serfass and co-workers for Research Project No. 2 of the American Electroplaters' Society. The user is referred to their publications.⁹⁹

Brighteners and Other Addition Agents. Methods of analysis of proprietary brighteners and addition agents are furnished by the vendors of proprietary processes.

ANODES

Since about 1915 improvements in nickel anodes—have kept pace with changes in solution composition and operation. This progress has been necessary, because solution and process changes have demanded improvement in that important phase of nickel plating. Whereas the impure 90 to 94% or the 95 to 97% nickel anode was satisfactory in the cold, low speed nickel bath of thirty-five years ago, it would fall to pieces in the modern Watts or bright nickel bath. The modern 99% pure nickel anode would have remained passive in the old low chloride cold bath of 1915. Furthermore, the impurities, such as iron in large

amounts, in the low purity anode are now known to be harmful to the operation of the modern baths.

With the introduction and widespread use of the Watts bath, the 90% nickel anode gave way to the 99% chill-cast nickel anode. Next came the 99% rolled, depolarized anode containing nickel oxide in small amounts. This anode corrodes smoothly, forming a light brown film which washes off as it is formed. Since small amounts of loose nickel are formed on corrosion in the Watts bath, anode bags are generally found necessary to prevent formation of nodular deposits as a result of the physical inclusion of these particles. This 99% rolled anode is widely used in high pH baths.

After the rolled depolarized anode, for certain applications came the cast carbon-nickel and, still later, the rolled carbon-nickel anodes. Both of these anodes contain in excess of 99% nickel and have the feature of forming their own "bag" on corrosion. This "bag" consists of a rather tenaciously adhering but porous carbon-silica film that holds back loose anode particles provided that they do not form in excessive amounts. These high purity, carbon-type anodes are used only when the pH of the bath is 4.0 or lower and are also supplied with cotton bags wherever possible.

Anodes cut from electrolytic nickel sheet have been used to a limited extent.^{100, 101} Several patents have even been issued for introduction of corrosion-promoting sulfur into the electrolytic nickel by adding suitable organic or inorganic sulfur compounds to the refining electrolyte. A recent suggestion¹⁰² is 0.005 to 0.03% sulfur be codeposited with the nickel from a bath into which sulfur dioxide is being introduced. The nickel is annealed at 816 to 982°C for 20 to 30 min to make an anode with good activity up to pH 5.5. The further introduction of 0.01 to 0.10% copper with and without 0.02% carbon, from copper sulfate and acetylene in the electrolyte, is said to permit the inclusion of as high as 0.12% sulfur and the satisfactory use of the unannealed anode at pH 1.5 to 5.5.

The corrosion behavior of an anode depends on the pH and the chloride content of the bath. The uniformity of corrosion (sometimes called anode activity) should not be confused with anode efficiency. Only a small chloride content, 2 to 3 oz/gal nickel chloride, is necessary to make the latter 100% for all types of nickel anodes under ordinary plating conditions, but the uniformity of corrosion and the amount of loose nickel formed may be markedly affected by an excess of chloride. Pinner¹⁰⁰ found that smooth corrosion of pure electrolytic-nickel anodes is obtained only if a high chloride ion concentration is present, the amount needed being less the lower the pH of the electrolyte. With

cast anodes the smoothness of corrosion improves with increase in chloride content only in the low range. Pinner and Borchert¹⁰³ observed excessive amounts of loose nickel due to grain boundary attack when the nickel chloride content was raised above 8 oz/gal. This limit does not apply to rolled carbon-type anodes which appear to suffer no ill effects from high chlorides. The same authors¹⁰³ show that slag inclusions and pipes or blowholes result in excessive formation of loose nickel and even crumbling of the anodes.

No fixed rule can be made for what constitutes an excessive amount of loose nickel particles from the anode without defining also the bath being used, the methods of operation employed, and the results expected. Pinner and Borchert¹⁰³ set a limit on permissible loose nickel at 0.04%, above which the carbon-silica film was shown to be incapable of holding the nickel particles at the anode without the use of cloth anode bags.

The exact relationship between chloride ion concentration and anode efficiency and current density has not been determined. The indications are that the electrolyte should be at least 1 N in chloride (equivalent to 15.8 oz/gal $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) for operations at anode current densities of 100 to 200 amp/sq ft and 2 N at 1000 amp/sq ft if 100% anode efficiency is to be maintained. Of course, the temperature, pH, degree of agitation, and perhaps other factors also influence anode efficiency.

PREPARATION OF BASIS METALS

POLISHING AND BUFFING

A decorative nickel finish has lasting beauty and utility proportional to the protection it affords the basis metal upon which it is plated. Numerous attempts have been, and are being, made to produce a substantially non-porous nickel deposit, but this goal has not been fully achieved. At the present time a considerable amount of experimental work is being directed toward finding the effect of metallic impurities in the plating solutions on the corrosion-resistant properties of the nickel plate. These considerations are covered elsewhere in this chapter. Such work has great importance, yet equal emphasis must be given to the effects of the basis metal and its surface characteristics, composition, and structure on the protective value of nickel plate.

Proper preparation of articles to be plated with nickel starts with the manufacture of the basis metal. Many investigators show that rolling seams, slag inclusions, blowholes, sand inclusions, and the like

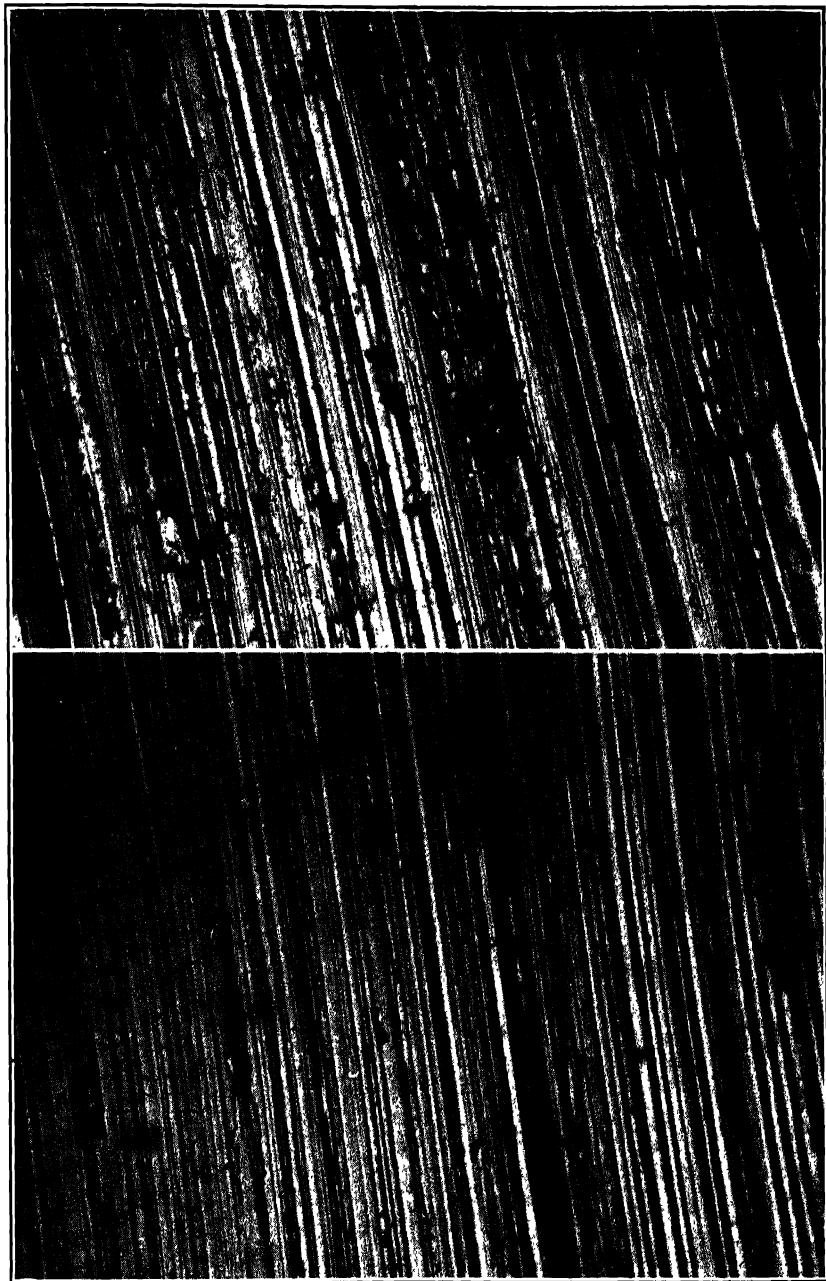


Fig. 7. Polish-scratch appearance of steel produced with No. 180 grit belt. Top, without lubrication; bottom, with lubrication. $\times 500$.

have a pronounced effect on the corrosion-resistant properties of nickel plate.¹⁰⁴ Also, the manner in which the metal is processed, either before or after being formed into articles of manufacture, has been proved to affect the porosity of the nickel deposit. For example, Thomas and Blum¹⁰⁴ and Maenaughtan and Hothersall¹⁰⁵ have shown that rough surfaces have lower hydrogen overvoltages than

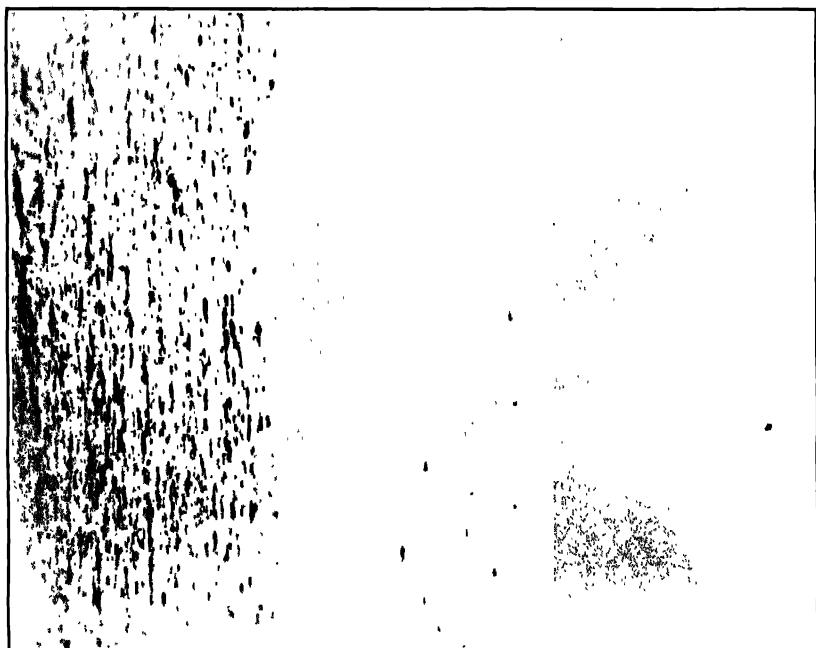


Fig. 8. Effect of basis metal polishing on roughness of subsequent nickel plate. At left, No. 90 grit dry; in middle, Nos. 90 and 150 grits dry; at right, No. 90 grit dry, Nos. 150 and 220 grits greased.

smooth surfaces and, therefore, are more susceptible to pitting. Cymbaliste¹⁰⁶ demonstrated how porosity may develop from scratches and fissures. Hothersall and Hammond¹⁰⁷ showed that rough machining, filing, and sand blasting increase the porosity. Phillips¹⁰⁸ found that a good quality auto-body sheet steel received a more impervious nickel coating if it was not polished. Pinner¹⁰⁹ showed the effects of polishing with different-sized grits. In general, his results show that rough grinding was detrimental to the protective value of nickel plate. He confirmed Phillips' results and extended them to indicate that smoothing out and rounding off the tops of scratches, as, for example, with a well-lubricated, final polishing wheel, was extremely

important from the standpoint of promoting the protective value of nickel.

Recent unpublished work may perhaps explain, at least in part, these findings. Figure 7 shows, at the top, the polish-scratch appearance of steel produced by grinding with a No. 180 grit belt without lu-

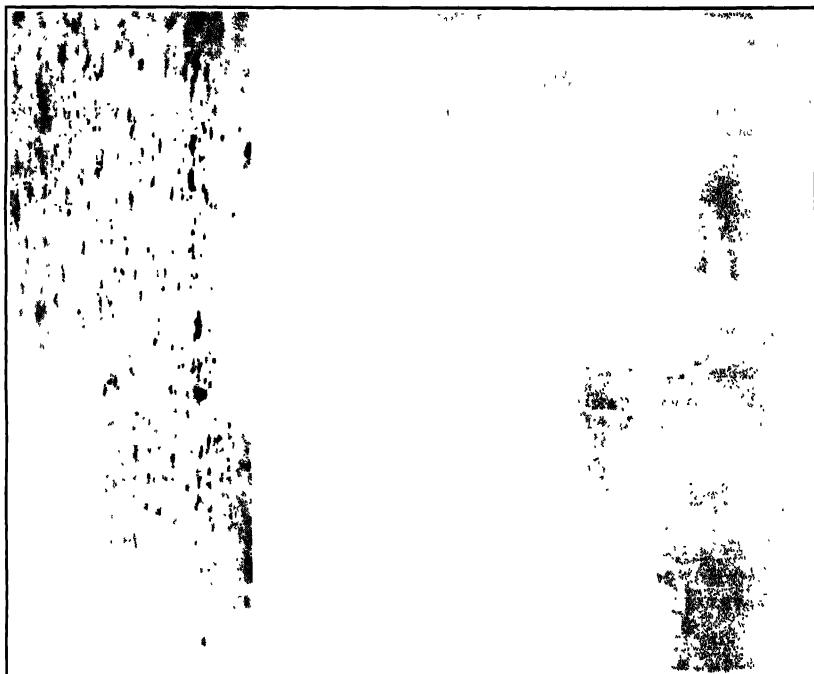


Fig. 9. Effect of basis metal polishing on roughness of subsequent nickel plate. At left, No. 90 grit dry; in middle, Nos. 90 and 150 grits dry, No. 180 grit greased; at right, Nos. 90 and 150 grits dry, Nos. 180 and 220 grits greased.

briation. The torn condition of the metal, with apparently many sharp scratch tops and loosely attached steel slivers, can be seen. At the bottom, Fig. 7 shows a surface polished in the same manner except that lubrication was used during the finishing operation. The changed character of the metal makes it appear more receptive to a nickel deposit having superior properties, and corrosion tests verify that interpretation.

In addition to promoting corrosion-resistant nickel plate, a good grease wheel or greased belt finish is important for the production of a smooth nickel plate. Figures 8 and 9 show the effect of basis metal polish on the roughness of subsequently applied nickel plate. Here

again one notes the effect of the proper condition of the basis metal on the properties of the deposit, independent of the plating department operations. The use of greaseless compositions, consisting of intimate mixtures of polishing grain and glue,¹¹⁰ is gaining in favor.

Because of the high cost, steel is seldom buffed prior to nickel plating. Where a buffed surface is required, it has been common practice to apply a copper plate and buff it. Brass, zinc alloy die castings, and aluminum alloys are usually buffed after any required polishing. Small parts are often both rough- and fine-finished by tumbling. Several new methods have been developed recently to produce fine finishes at relatively low cost.

ELECTROPOLISHING

One important finishing method which has recently come to the fore is electropolishing or, perhaps better, electrobuffing. It is used either as an adjunct to polishing, when it also serves to remove scratch tops and slivers (see above), or by itself where the original surface condition and finish requirements permit.

According to Faust¹¹¹ low carbon steels such as S.A.E. 1010 and 1020 can be smoothed and made quite lustrous, but the appearance might suffer from non-metallic inclusions, scams, orange peel effects, etc. S.A.E. 1040, 1060, 1085, 4130, 4140, and 5110 Nitrallloy, as well as nitrided and carburized steels, electropolish to a high luster, the appearance depending upon the quality of the steel. The only commercially used bath is of the sulfuric-phosphoric acid type.¹¹² Cast or malleable iron has not yet been electropolished satisfactorily.¹¹³ Zinc, zinc-base die castings, and magnesium alloys are not known to be electropolished commercially.¹¹⁴

Faust¹¹¹ states that efficient baths of undisclosed composition are available for economical electropolishing of lead-free brasses. Berger¹¹⁵ reports good commercial results with rather complicated baths containing phosphoric, chromic, sulfuric, propionic, and hydrofluoric acids plus sodium dichromate on relatively small brass stampings containing up to 1% lead.

Wrought aluminum alloys 2S, 3S, 14S, 24S, 51S, 53S, and 64S are electropolished commercially in a sulfuric-phosphoric-chromic acid bath,¹¹⁴ according to Faust,¹¹¹ who also lists a number of other patents for electropolishing aluminum, including one¹¹⁵ for die-cast aluminum alloys containing silicon, which do not polish well in the aforementioned bath.

Considerable general cost data and information about limiting factors in electropolishing are available.¹¹⁶

CLEANING AND PICKLING

The purpose of cleaning prior to plating is to remove all interfering substances from the surface to be plated. Adhesion, smoothness, and corrosion resistance of nickel plate depend upon a proper cleaning cycle. The desired maximum adhesion of nickel is obtained when the deposited metal is so close to the subsurface that atomic forces come into play. Diffusion of one metal into the other (alloying) is not necessary for adhesion and may be detrimental if the alloy layer or any part of it is weaker or more brittle than the individual metals. Any foreign substance which separates the coating from the subsurface decreases the adhesion. Such substances may be oxides or graphite in or on the surface, basic salts precipitated on immersion in the plating solution of work with an alkaline film, and oils and greases from the rolling mill or from the polishing or buffing operation. When such substances are present, the coating may be separated cleanly from the subsurface.

Sometimes part of the subsurface stays attached to the coating, or part of the coating stays attached to the subsurface when the coating is pulled off. In the former case, the subsurface has ordinarily been cold worked prior to plating and the cold-worked layer was or became embrittled by hydrogen absorption during the cleaning or plating operation. In the latter case, either an intermediate coating is inherently weak and inclined to rupture or an easily embrittled alloy layer was formed, diffusion having been made easier because of previous cold work having imparted much energy to the surface. The removal of the worked surface prior to plating solves this problem. These effects are discussed by many authors, brass being covered by Hothersall and Hammond,¹⁰⁷ steel by Hothersall¹¹⁷ and by Zapffe and Faust,⁴⁸ and zinc die castings by Lewis¹¹⁸ and by Oplinger.¹¹⁶

The cleaning procedure should also eliminate any particles from the surface which may cause roughness of the subsequent plate. This is important in dull nickel plating, because subsequent buffing or brushing tears out such particles and, also, the nodules of plate deposited over them. Holes are made in the coating, and its corrosion-protective value is decreased. In addition the cost of buffing a rough surface is much higher than that of buffing a smooth surface. Since the final surface must be smooth, the necessity of avoiding roughness in bright nickel plating is obvious.

Very fine particles of oxide residues or buffing dirt must also be removed even if they do not greatly interfere with either adhesion or smoothness. They may constitute nuclei for locally intensified gas evolution, which causes pits that reduce the corrosion protection and affect the luster of bright nickel coatings.

Up to a few years ago most electrocleaning was being done with the work as cathode, because that provides the maximum amount of agitation at the surface, twice as much hydrogen being evolved at a cathode as oxygen at an anode. Lately, anodic cleaning has come to the fore, primarily because it gives more complete smut removal. For die castings in particular, it removes the outermost, easily embrittled layer of buffed metal without leaving smut on the surface. Anodic cleaning is also preferred on other metals, because any metal which has gone into solution is not redeposited to interfere with adhesion.

With few exceptions, the parts to be plated are given an acid treatment subsequent to the cleaning operation, the purpose being to remove oxides and tarnish films that would prevent adhesion, and also to dissolve the outermost layer of polished metal. Commercial hydrochloric acid, so-called muriatic acid, in varying concentrations is most commonly used. A high concentration, up to 50% by volume, is used on steel; a medium concentration of about 10% by volume on copper and brass; and a low concentration, 1 to 5%, on zinc and zinc die castings. Sulfuric acid is also employed, especially to neutralize the alkaline film present on copper undercoatings deposited from a cyanide bath. Brass and copper parts are sometimes cleaned in sodium cyanide solutions, preferably containing some caustic soda to prevent rapid decomposition.

Adhesion is damaged by a fatty acid film which can form, on the surface of cleaned metal, by the reaction of soap from the alkaline cleaners with the subsequent acid dip. In order to minimize or eliminate the formation of such films, a double cleaning cycle is used in large installations. In it, the parts are usually cathodically cleaned, acid dipped, anodically cleaned, and given a second acid dip, with the usual rinses. Such a procedure results in a minimum of soap buildup in the anodic cleaner. Both cleaners may be operated anodically, but initial cathodic cleaning is preferred, especially if the work is fairly heavily coated with oil. Then the greater turbulence by liberated hydrogen is employed to advantage.

For steel parts the use of an anodic acid etch, long employed by the British, is rapidly gaining in favor as a preparation for excellent adhesion. Such baths are composed of substantially concentrated sulfuric acid and may contain addition agents such as glycerin. In oper-

ation, the previously cleaned parts are made anodic at current densities of about 200 amp/sq ft.

The basis metal is frequently copper plated prior to nickel plating. Such a procedure is practically universally used on zinc and zinc-base alloys. Although nickel plating baths had been designed for plating directly on this metal, continued difficulty was encountered with adhesion to the zinc, and with contamination of the plating solution by zinc that dissolved before plating started or through pores in the coating during plating. Now copper is deposited of sufficient thickness to form an alloy layer with the zinc and provide additional copper which remains unalloyed under the nickel.

As suggested by Schlötter¹¹⁹ and confirmed by Maenaughtan and Hothersall,¹⁰⁵ copper from a cyanide bath covers imperfections in the steel surface better than does nickel plate and thereby reduces porosity. Recent A.S.T.M. corrosion tests, however, have indicated that copper has little protective value on weather exposure and might be detrimental to corrosion protection. These results to date are considered tentative only, because some actual service tests appear contradictory to the A.S.T.M. weather-exposure data.

For plating of aluminum, magnesium, and their alloys, the cleaned parts are coated with adherent zinc films by chemical displacement. Copper is then plated and is followed by nickel, as in the case of zinc alloys.

A film of zinc between the aluminum and the outer coating of copper, nickel or other more noble metal may lead to blistering upon exposure to a corrosive environment. This tendency can be avoided by anodic treatment of the aluminum in phosphoric acid solution.^{120,121} The thin anodized layer has a critical thickness and is partially removed upon entry into a nickel plating bath and at start of the deposition. Unfortunately, the anodic phosphoric acid process is applicable to only a few aluminum alloys in addition to 2S and 3S.

Magnesium and its alloys may be plated with nickel by using a special type of zinc-immersion process recently described by De Long.¹²²

FINISHING NICKEL DEPOSITS

Nickel plate is used in a variety of finishes, including bright, semi-bright, matte, and butler finishes. The methods of producing them are not considered a proper topic for this discussion. In general, the use of buff wheels, scratch-brushes, and the like has been widely known for years. It is considered of consequence, however, to mention in some detail a procedure which is receiving increasing attention at this time.

Reference is made to the electrochemical finishing of nickel by electro-polishing (electrobuffing). This process involves the anodic treatment of nickel at fairly high current density in concentrated acid baths, which consist of sulfuric acid with¹²³ or without^{121, 125} glycerin or other additions or, better, mixtures of sulfuric and phosphoric acids^{126, 127} possibly with aluminum salts¹²⁸ or hydrochloric acid¹²⁹ or mixtures of phosphoric and chromic acid.¹³⁰ Information about these processes is available in widely published articles by Faust,^{111, 131} Wernick,¹³² and others. The amount of electrolysis required to effect full luster is a function of the structure of the plated nickel, fine-grained deposits requiring a smaller amount than coarse-grained deposits. For example, the bright and semi-bright deposits may be electrobuffed with the removal of perhaps 0.0001 to 0.0003 in. (0.0025 to 0.0075 mm) of metal, whereas a dull deposit from a Watts plating solution may require the removal of as much as 0.001 in. (0.025 mm).

Such processing replaces wheel buffering operations only to the extent that brightening of the metal is secured, but the improvement in appearance, as far as basis metal scratches are concerned, is not realized to the same extent as with mechanical buffering. Electrobuffing removes nickel more uniformly from the surface of parts of involved contour than nickel is deposited by plating. This constitutes a limitation of the process because excessive thicknesses must be applied during plating in order to leave a sufficient thickness in the low current density areas after electrobuffing. As of this writing, therefore, the process appears to be most advantageously applied to parts where brightening only is desired and where the shape is such that the last-mentioned limitation is of minor consequence.

TESTS OF DEPOSITS AND SPECIFICATIONS

The protection afforded a basis metal by nickel deposit depends on a number of factors, some of which are not wholly understood. Many of them have been, or are being, investigated, and, in time, all will be brought under control so that effective specification requirements can be written for each.

POROSITY

Porosity is a well recognized factor, and most specifications call for a porosity test, usually the salt spray test.¹³³ However, as shown by Thon and Addison,¹³⁴ this and other chemical tests can be used to detect only a portion of the "gross" porosity, caused by non-uniformity of the basis metal surface being plated, dirt in the plating solution, or

other accidental factors. Many such pores are likely to cause perforations. Thon and associates^{135,146} have also discovered a structural porosity, or gas permeability. This permeability decreases rapidly with increase in thickness of the deposit, becoming too low to measure at a thickness well below 0.001 in. (0.025 mm). In the experiments with thin foils, the permeability increased rapidly upon exposure to a corrosive atmosphere. At this writing it is doubtful that the permeability has commercial significance.

CHEMICAL RESISTANCE AND CRACKING TENDENCY

Pores also form when the plated article is in service, both by corrosion pitting and by cracking due to unfortunate combinations of low ductility and high internal stress, especially when high external stress is also present. Bath impurities which in some form enter the deposit, and also the brighteners and other addition agents present in the electrolyte, can affect adversely both the chemical resistance and the cracking tendency of a nickel deposit. At the present time, there are no specific inspection tests for chemical resistance, although rapid failure in the salt spray test is believed to be caused by both of these faults.

Heussner and co-workers²⁹ have suggested slow bending as a rough shop test for plated sheet metal. At the point of cracking of the coating, the unit elongation, which is used as a measure of ductility, is approximately $T/2R$, where T is the total thickness of base metal and plate and R is the radius of curvature of the bend. Phillips and Clifton¹³⁷ used a modified Ericson cup test for the same purpose. None of these tests is suitable for articles with heavy sections, but possibly a modified Brinell test might be used for them in a manner similar to that of the Ericson test.

No inspection test has been developed for internal stress in coatings on commercial shapes.

NATURE OF BASIS METAL

It is important to note that the condition of the surface underlying the nickel deposit has a bearing on the performance of the coating. In outdoor exposure, Anderson and Reinhard¹³⁸ found indications that buffed brass in a pore is anodic to nickel, whereas unbuffed brass is cathodic to nickel and is sacrificially protected by it. Similarly, Graham¹³⁹ observed that the cleaning cycle employed on buffed copper plate prior to nickel plating affected the kind and amount of corrosion

product seeping through what was believed to be crack pores in copper-nickel-chromium deposits on steel. These preliminary findings, of course, have not yet had an influence on specification requirements.

THICKNESS

Outdoor exposure tests amply demonstrate that one way of reducing porosity is to apply coatings of greater thickness.¹⁴⁰⁻¹⁴³ These tests have also shown that the protection afforded by nickel coatings depends greatly on the corrosiveness of the atmosphere. For a summary of this work, the reader is referred to the chapter by Wesley in the *Corrosion Handbook*.¹⁴¹

ADHESION

Adhesion to the basis metal is another factor in the performance of decorative nickel coatings. Methods of measurement have been examined by Ferguson and co-workers.¹⁴⁵ The most commonly used is the grinding wheel test, in which a rough emery wheel is made to cut in a jerky fashion from the basis metal into the deposit to loosen the latter if it is non-adherent. Such a test does not lend itself well to specification purposes. Mesle's or Jacquet's peeling test as modified by Brenner¹⁴⁶ has at least semi-quantitative significance. In this test a handle is attached by electrodeposition of heavy nickel to the original coating and serves to initiate the peeling. The required force F is measured in kilograms per centimeter of width of strip, and a significant constant $F/T\%$ is calculated, where T is plate thickness in centimeters. Further work may possibly make it applicable to specification testing.

APPEARANCE

The saleability of a plated product depends to a large extent on its appearance. No specification tests have appeared as yet, and the work being carried out by Committee B-8 of American Society for Testing Materials on this subject has shown it to be very complicated.

SPECIFICATIONS

The importance of thickness and of gross porosity has led to the adoption, by the American Society for Testing Materials and the American Electroplaters' Society, of specifications covering these prop-

erties. Such specifications are now available for nickel coatings on steel,¹⁴⁶ on zinc and zinc alloys,¹⁴⁷ and on copper and copper alloys.¹⁴⁸ The standard requirements for the different grades of coatings are summarized in Table 1.

A standard testing method for nickel which involves sectioning of the deposit and thickness measurement is described in a separate A.S.T.M.-A.E.S. specification.¹⁴⁹ It permits the use of the non-destructive magnetic test by Brenner for nickel coatings applied on non-magnetic and on magnetic surfaces.¹⁵⁰ The test has lately been modified to permit its use also with a non-magnetic coating, such as copper, between the nickel and a magnetic basis metal.¹⁵¹

Industry, especially the automotive industry, has followed the A.S.T.M.-A.E.S. specifications with only minor variations. Novelty goods and the like, however, are frequently plated to lower specifications (or to none).

Nickel deposits for industrial purposes depend for their value largely on tensile properties and adhesion. Tensile properties are usually gaged by means of a hardness test on a Vickers or Knoop machine; adhesion by the modified Ollard tests,¹⁵² in which a specially prepared test piece is subjected to a tensile test.

HEAVY NICKEL PLATING

"Heavy nickel plating" implies the application of thick nickel deposits for industrial uses and has a connotation analogous to the term "hard chromium plating." Deposition of nickel for resistance to process industry corrosion, for combined corrosion and wear resistance, for salvaging worn or mismachined parts, and for direct electroforming of finished metal shapes are all included. The thicknesses of nickel involved in such applications range from 0.003 in. (0.075 mm) to the extreme realized recently in a structural unit weighing 70 lb which was electroformed with a wall thickness of 0.5 in. (12.5 mm).¹⁵²

BATH TYPES

Choice of plating bath compositions is dictated primarily by the mechanical properties desired in the deposit, and to a lesser degree by such considerations as smoothness of deposit, tendency to form nodules and trees, stress in the deposit, and ease of control of the process. A good discussion of methods, special precautions for, and applications of, heavy nickel plating is available.¹⁵³

SOFT NICKEL

For applications requiring utmost ductility, the Watts bath is used under the conditions outlined on pages 303 to 308. At pH 4 to 4.5, a temperature of 54°C, and a current density of 50 amp/sq ft an elongation of 37% in 1 in. (25 mm) can be obtained. Annealing for 15 min at 760°C increases the elongation to 55%, which is more than sufficient for severe commercial forming or drawing operations. Care must be taken not to overanneal, since this causes large grain growth and marked loss in ductility. A word of caution regarding impurities should also be inserted here. Very small amounts of lead codeposited with nickel do not alter the as-plated ductility but have a pronounced embrittling effect if the nickel is heated. As little as 0.02% lead may have a noticeable effect. Variations in the plating conditions cause variations in the mechanical properties of the deposit in the directions set forth on pages 309 and 310.²⁷

HARD NICKEL

Bath F of Table 2 is a good electrolyte from which to deposit thick layers of nickel of controllable hardness in the range of 350 to 500 Vickers hardness. This bath was found by Wesley and Roehl,^{154,155} to produce nickel with a tensile strength of 152,000 lb/sq in. (106 kg/sq mm), a hardness of 425 Vickers, and an elongation of 6% in 2 in. (50 mm). By varying the pH and the temperature within the limits given in Table 2, the desired hardness can be obtained. The tensile strength increases and the ductility decreases with an increase in pH and a decrease in temperature.¹⁵⁴ The deposit has a rather low annealing temperature and will not retain full hardness above 232°C. If a heavy deposit with an extremely hard surface is required, a layer of hard nickel followed by chromium is employed. Disadvantages of the hard nickel bath are: a greater tendency to form nodules and trees than the chloride or Watts bath; and a high internal stress in the deposits.

CHLORIDE BATHS

Blum and Kasper²¹ worked with an all-chloride nickel bath operated at the boiling point. Later, Wesley and Carey¹⁶ made a careful study of the chloride-boric acid electrolyte G of Table 2 and the properties of its deposits. They showed that this bath offers the advantages over the Watts bath of a 50% reduction in tank voltage and power consumption, ease of control due to simple composition, wide plating range, high anode and cathode efficiencies, lower susceptibility to pit-

ting, smoother and tougher deposits, less tendency to form nodular growths and trees on thick deposits, and production of coatings which are easier to buff. The greater corrosiveness of this electrolyte is no longer a serious disadvantage with the corrosion-resistant equipment now available, but its tendency for rapid rise in pH and the high internal stress in its deposits are real disadvantages. Nickel from bath G (Table 2) has moderate hardness (230 to 260 Vickers), tensile strength (about 100,000 lb/sq in.), and elongation (20% in 2 in.).¹⁶

The disadvantages of the chloride bath are reduced by mixing it with a sulfate bath to produce Pinner and Kinnaman's¹⁷ bath H of Table 2. This electrolyte retains many of the advantages of the chloride solution. It is finding use as a high current density bath for decorative bright nickel plating and also for rapid buildup of extremely heavy deposits in the salvage of worn parts. For high speed bright decorative plating, appropriate organic addition agents are added to the bath, which otherwise retains its desirable properties.

Another low resistivity solution used in depositing a rather hard nickel of unusually high tensile strength is bath J (Table 2).¹⁵⁶ It is said to be ideally suited for stereotype plating at the relatively high current density of 40 amp/sq ft. Its chief handicaps are the volatility and odor of the acetic acid buffer. Little information has been published on this bath.

CORROSION AND WEAR RESISTANCE

Any of the above-mentioned heavy nickel electrolytes may be used in depositing thick nickel coatings on process equipment to resist corrosion or combined corrosion, wear, and fatigue. Nickel-lined steel pipe is available commercially and is in service in corrosive oil wells and in the chemical industry. An old application is the coating of huge, highly polished, cast iron drums used in manufacturing photographic film. The degree of polish required in this service is so high that it cannot be attained with wrought metals because they contain non-metallic inclusions which cause tiny pits upon buffing. The coatings now used on these drums are deposited from a high chloride, Watts-type bath under conditions giving nickel of moderate hardness. Nickel-lined food-processing kettles, nickel-coated paper mill rolls, and nickel-coated filter presses for viscose rayon solutions are outstanding examples of heavy nickel plating on large units.

In applications where steel tends to fail by corrosion-fatigue, a nickel coating has a great beneficial effect;¹⁵⁷ for example, the life of sucker rods in corrosive oil wells is lengthened many times by appli-

cation of 0.006-in. nickel coatings¹⁵⁸ from the Watts bath. Nickel coatings seem to be particularly effective in preventing "fretting corrosion," a phenomenon which is not well understood.¹⁵⁷

Hard nickel is generally specified for applications involving wear. However, the performance of nickel from the other baths is better than might be anticipated, because this metal work-hardens rapidly under sliding action. Thus the life of hardened-steel, gasoline pump gears which fail by seizure and dragging was multiplied more than fivefold by application of 0.0002 to 0.0003 in. nickel from the chloride bath G (Table 2). For the most severe conditions of contact with steel under a high pressure, it is preferable to use a duplex deposit consisting of nickel with a few thousandths inch of chromium.

RESIZING

The long-standing British practice of building up worn or mismachined parts by heavy nickel plating¹⁵⁹ is in use in this country on a modest scale, particularly in connection with the maintenance of trucks, buses, and airplanes. There is nothing unusual about the nickel plating operation itself, the bath being selected to give nickel deposits of the desired mechanical properties. Preparation of the basis metal to guarantee perfect adhesion, setting up the anodes, and stopping off or shielding the work to secure good metal distribution can be exacting. They are described in a bulletin issued by the British Armament Research Department.¹⁶⁰

There are numerous advantages in using nickel for salvage: it can be deposited rapidly, uniformly, and economically; the metal can be ground and, in addition, it can be machined by conventional methods; it is corrosion resistant and tough, and it withstands shocks. Where heavy deposits with an extremely hard surface are required, it is good practice to make up the major portion of the desired thickness with nickel and then finish with several thousandths of an inch of chromium.

ELECTROFORMING

A recent publication¹ reveals an impressive accumulation of literature on electroforming which recounts the commercial production of a long list of articles ranging in size from hypodermic needles to burial caskets. Electroforming has inherent advantages over other processes of fabrication for parts which (a) require a very high surface finish, especially on internal surface contours, (b) require high precision in

certain dimensions, (c) incorporate intricate details, and (d) are needed in quantities too small for die-casting runs.¹⁶¹

Copper is the most favored metal in quantity of product, but nickel is prominent wherever its greater strength, toughness, hardness, or corrosion resistance is needed. The principal factor which retards the application of nickel in fabrication by electroforming is the residual stress in nickel deposits, which may cause warpage of the product. The subject of stress in nickel deposits and the outlook for reducing it are discussed on pages 348 and 349. A common current practice is to apply a layer of nickel to the surface of the mold in starting electro-forming, then to build up to the desired thickness with copper. The nickel layer thus is in a position to supply wear and corrosion resistance plus some stiffening of the object, yet is not permitted to become so thick as to cause too much distortion by internal stress.

Electrotypes are the oldest kind of electroformed article. The plate itself is commonly started on a lead, wax, or plastic mold by applying a layer of nickel 0.0005 to 0.002 in. thick from bath A of Table 2. It is then built up with copper and stripped so that the nickel layer forms the working surface. This procedure gives electrotypes which produce a larger number of printed impressions than plates of copper which have been stripped from the wax and then nickel-faced. A moderately hard, tough nickel from the Watts bath or bath J (Table 2) is also commonly deposited on stereotypes to a thickness of 0.0005 to 0.001 in. to improve their performance. If the Watts bath is used, it is made more dilute and operated at a high pH of 5.8 to 6.0 (colorimetric) to secure harder deposits.¹⁶² Ledford¹⁶³ has disclosed that the following bath is being used commercially to produce, on electrotypes, nickel deposits of high hardness combined with good ductility and high permissible current density without distortion of the forms: nickel sulfate 32 oz/gal, nickel chloride 3 oz/gal, boric acid 4 oz/gal, ammonium sulfate 0.2 oz/gal, nickel formate 2 oz/gal, and cobalt sulfate 0.35 oz/gal; Ledford also reports that it is being operated at pH 4.7, 49°C, and 50 amp/sq ft with anodes containing 1% cobalt.

Another old application of electroforming, and one which illustrates perhaps better than any other its ability to reproduce faithfully the details of the mold surface, is the making of phonograph record matrices and stampers. The process is described in detail in Chapter 8. Here, again, a nickel surface layer is incorporated for improved wear resistance, retention of surface markings, and resistance to corrosion, while the body of the part is formed of copper to avoid warpage due to stress. The nickel layer is generally only 0.0003

to 0.0005 in. thick, and there seems to be little uniformity in the plating conditions employed. Cathode rotation is generally provided, and the plating temperature is kept low. Some plants still employ an old, low pH, double salt bath containing magnesium sulfate from which nickel is plated at the low current density of 5 amp/sq ft. In at least one modern plant, nickel is deposited rapidly from a modified bright nickel bath at 30 amp/sq ft to get a very hard deposit. After removal from the mold, chromium is commonly applied to the nickel face of the stampers to a thickness of 0.00005 to 0.0001 in. This amount of chromium can be applied to the sound track without significant loss of fidelity.

Important military applications of nickel electroforming include pitot tubes for air speed indicators, precision tubing of rectangular cross section, and fittings for radar, wave guides, computing cams, large searchlight reflectors, constant mesh screens, and venturi tubes used in the jet propulsion program.¹⁵² A fully automatic machine for electroforming fountain pen caps of nickel has recently been developed.¹ The problems involved in electroforming plastic dies and casting dies are being studied intensively owing to the high cost of hobbing such dies out of solid metal.¹⁶¹ Molds for machine molding of elastic toys and dolls are being made of nickel by electroforming by a process similar to that devised for making molds for artificial hands.¹⁶⁵

MACHINING

Soft and hard nickels can be readily machined if suggested speeds, feeds, and tool rakes are adopted. The subject is discussed in recent publications.^{166, 153}

HEAT TREATMENT

The general practice in England¹⁵⁹ (and it is recommended where feasible) is to subject heavy nickel deposits to a low temperature treatment to improve adhesion, expel hydrogen, and, in some cases, reduce stress. The time and temperature have not been standardized, but they vary from $\frac{1}{2}$ to 3 hr at 150–290°C. Deposits from the hard bath cannot be heated above about 204°C without some loss in hardness.¹⁵⁵

STRESS IN NICKEL DEPOSITS

A mysterious, yet important, characteristic of nickel deposits is that all are formed in a condition of internal contractile (tensile) stress ex-

cept when one of certain specific organic addition agents is present. The study of this phenomenon received a great impetus in 1946 from the outbreak of spontaneous cracking of bright nickel deposits in the automotive industry at a time when a maximum production rate was imperative. As a result several good papers appeared^{130, 137, 29, 167, 168} which teach how to measure such internal stresses quantitatively on specially prepared test pieces. All are based upon the measurement of amount of bending of a strip nickel plated on one side only.

THEORY

On the theoretical aspects, agreement has by no means been reached. The evidence in favor of a hydrogen theory was marshaled by Wyllie.¹⁰⁰ This ascribes the development of a tensile stress in nickel to deposition of an expanded form of nickel-hydrogen or hydride lattice at the moment of deposition followed by diffusion of the hydrogen out of the deposit and contraction to the normal nickel lattice. This idea was supported by the fact that the presence of some depolarizers and a-c superimposed on d-c plating current both reduce contractile stress, presumably by oxidation or evolution of hydrogen, before it can exert any considerable effect on the growing metal lattice. The hydride theory does not explain some of the experimental results, such as the marked increase in tensile stress produced by small amounts of certain impurities in nickel baths (iron, manganese, zinc, carbon dioxide, organic colloids) or the effect of certain organic addition agents in decreasing or reversing tensile stress.¹⁷⁰ This theory, that nickel hydride is formed, is now in disrepute for metallurgical reasons.¹⁷¹

Martin¹⁷² favored the idea of codeposition of nickel hydrate as a cause of stress without suggesting a mechanism by which such colloidal matter can induce a delayed contraction of the nickel lattice, but Hothersall¹⁷⁰ thought it likely that such occluded substances may be a cause of stress by such a mechanism as reduction of basic compounds by atomic hydrogen, corrosion, hydration or dehydration of colloids. He also suggested that both rapid and slow processes may be involved, those involving hydrogen being in the former class whereas hydration or dehydration would be in the latter class.

Soderberg and Graham¹³⁸ proposed a still different cause of tensile stress, namely that it is simply a manifestation of the greater internal energy content of the newly deposited metal equivalent to the over-voltage involved in deposition. An expanded lattice would have a higher energy content and would then tend to contract.

EFFECT OF BATH VARIABLES

Regardless of the theoretical mechanism by which stresses are set up, the practical plater will want to know how the major plating variables influence internal stress in nickel deposits. There is disagreement in the data of the papers on stress quoted above^{129, 132, 161, 163, 166} regarding the effects of some variables, but the preponderance of evidence supports the following conclusions with regard to stresses in nickel deposition.

1. Positive (tensile) stress increases with increase in chloride content of the bath.
2. The effect of temperature upon stress is not consistent; it varies with the composition of the bath (principally the chloride content) and the current density.
3. The effect of pH varies with composition of the electrolyte; however, for a Watts bath it is definitely advisable to keep the pH well below 5, not only because deposits with lower stress are obtained, but also because the harmful effects of some impurities on stress may be much more pronounced at pH 5 or above.
4. The effect of current density is not marked over the range 10 to 50 amp/sq ft but is usually in the direction of an increasing tensile stress with increasing current density.
5. Superimposing alternating current upon the direct plating current tends to reduce stress, other conditions remaining the same.
6. Agitation has little effect upon stress.
7. Evidence regarding effects of impurities and addition agents are conflicting, apparently because these effects change with variation in solution composition and pH. Hydrogen peroxide, carbon dioxide, certain organic brighteners of the second class, wetting agents, and iron, zinc, lead, and sodium salts can all act as stress raisers under some conditions. Ammonium sulfate reduces stress in high pH baths, but the reverse or no effect may occur at lower pH values.²³
8. Several types of addition agent, such as fluorides and fluoborates, tend to reduce tensile stress, and some, such as the brighteners of the first class, can cause the stress to pass through zero and even reverse in direction so as to make the nickel expand or be under compression if restrained from expanding. Unfortunately, these organic compounds or their decomposition products tend to affect the ductility of the deposit adversely. By exercising careful control and frequent purification their use in proprietary bright nickel baths is successful in practice.¹⁶⁴ A less important adverse effect should be mentioned.

It is encountered when nickel deposits, containing minute amounts of sulfur from the =C—SO— type of brighteners, are subjected to heating above 540°C, namely, a loss of ductility, called sulfur embrittlement.

STRESS VERSUS DUCTILITY

It is important to differentiate between the deleterious effects of high stress and lack of ductility. There is no predictable relationship among hardness, brittleness, and stress. Relatively soft deposits from the Watts bath may be highly stressed in tension and show good ductility, whereas nickel deposited in the presence of 0.67 oz/gal sodium naphthalene trisulfonate can show zero stress with a Vickers hardness of 540 and a low ductility.¹⁷⁰ A good case can be made for specifying a modicum of ductility, instead of a definite minimum stress value, as a criterion for avoiding danger of spontaneous cracking. A deposit possessing some ductility must suffer appreciable deformation before it will crack. If this deformation occurs spontaneously, that is, without externally applied stress, it will be in such a direction as to relieve the internal stress and to reduce the tendency to crack.

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Platinum Group Metals

K. SCHUMPELT*

The group of platinum metals comprises the following six:

Metal	Atomic Weight	Specific Gravity
Platinum	195.2	21.4
Iridium	193.1	22.4
Osmium	190.9	22.5
Palladium	106.7	12.16
Rhodium	102.9	12.4
Ruthenium	101.7	12.1

Of these six metals only platinum, palladium, and rhodium have found practical applications in the field of electroplating. Before 1915 and particularly during World War I, the price of platinum was comparatively high; therefore the use of this metal was limited to a few applications as a purely ornamental finish. This also explains why the literature on the deposition of the platinum metals has always been rather meager. Most of the information and formulas given in textbooks refer to platinum, and there are only indications that similar solutions could be used for palladium and rhodium.

When during the early years of this century white gold began to come into vogue, the jewelers very soon found themselves confronted with the serious problem that all the white gold alloys, particularly those which contained nickel as the whitening metal, discolored after a relatively short time. To overcome this serious drawback, the jewelry manufacturers resorted to flash-plating white gold articles with metals which promised to give some protection. Strange as it may seem, even chromium and tin deposits were used for this purpose on expensive white gold jewelry. Both metals, however, were objectionable, the former on account of the blue color and the lack of throwing power, and the latter because it stained light-colored dresses. The only logical solution of this problem was the use of platinum as a

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tarnish-preventing coating, and perhaps only the high cost of the metal at this time and the lack of reliable formulas for platinum plating solutions account for the delay in its general application.

After the discovery of a rich source of supply of platinum metals in certain Canadian nickel ores, the prices were lowered sufficiently to invite renewed interest of manufacturers and finishers.

Most applications of electrodeposited platinum metals today are for ornamental or decorative purposes rather than for protective purposes. Very little work, and that mostly experimental, has been done on electroforming with the platinum metals. In this field palladium seems to be the most promising of the six metals, owing to its low specific gravity and its low price. The main difficulty is the high affinity of palladium for hydrogen, a certain amount of which is always codeposited with the metal, causing warping or deformation of the electro-formed piece.

An increased demand for white and tarnish-resistant finishes since about 1940, together with a concurrent decrease in the cost of platinum metals, has stimulated the research work in this line, as is evidenced by the great number of patents¹ issued since 1927.

Rhodium, in particular, has found an ever-increasing number of applications as a finishing metal, despite its high price as compared with platinum and palladium. The explanation may be found in the hardness and brilliant bluish white color of the rhodium deposit and in the fact that rhodium plating solutions are easy to operate, are not very critical in regard to current conditions, and have excellent throwing power. As to future developments, it seems that rhodium will remain predominant over the other platinum metals. However, since the supply of rhodium is limited, it is desirable to improve the known platinum solutions and also to develop the use of plating palladium by itself or in combination with other metals. Atkinson² describes a method of codepositing palladium with either cobalt or nickel.

PLATINUM

The oldest known and most widely used platinum plating solution dates back to a French patent granted to Pilet in about 1883. In his formula platinum is present in solution as chloroplatinic acid, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (commonly referred to as platinum chloride). In preparing the bath this salt is boiled with sodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, and ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$, for a considerable time. During boiling, the color of the solution changes from

much below 6.4 may cause peeling, especially in the nitrate-nitrite bath.

Up to the present addition agents have not had much success in brightening the deposit. In this connection it must be remembered that most organic substances, when added to the bath, will eventually reduce the platinum compounds to the metal. Platinum anodes are used in all baths. The basis metals to be plated should be cleaned in the usual manner by electrocleaning and by cyanide or acid dips or both.

For reasons of economy it has become common practice to apply a nickel undercoat. This is necessary whenever lead, tin, and zinc alloy articles are to be plated. Since platinum deposits are used mostly for ornamental purposes and as flash plates, no special thickness tests are needed and no specifications have as yet been set up. The only exception is in the case of white gold jewelry. Whenever the word "platinum" appears in the hallmark, the stamping law requires a platinum deposit of 5% by weight of the article. When heavier than flash deposits of platinum are applied, they have to be scratch-brushed intermittently. Owing to the codeposition of hydrogen, platinum deposits are, as a rule, hard and brittle and therefore difficult to polish. The buffing wheel should be charged preferably with an aluminum oxide or a chromium oxide compound.

PALLADIUM

The oldest practical formula for a palladium plating bath is given in a patent by Pilet⁶ (1844) which is analogous to his formula for a platinum plating bath.

PILET PALLADIUM BATH

Palladous chloride, $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$	0.5 oz/gal (3.7 g/l)
Disodium phosphate, Na_2HPO_4	13.4 oz/gal (100 g/l)
Diammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	2.6 oz/gal (20 g/l)
Benzoic acid, $\text{C}_7\text{H}_6\text{O}_2$	6 dwt/gal (2.5 g/l)

This solution is boiled until the dark red color is changed to a light yellow, indicating the formation of a complex ammino palladium compound.

Palladium deposits can be obtained from this solution at 50°C and at about 1 to 2 v, and a current density of 1.8 to 2.8 amp/sq ft. Under these conditions the deposit remains bright for short plating periods but soon becomes cloudy and dull. Platinum or palladium anodes are used, neither of which are attacked. Palladium is replenished in the

bath through additions of palladous chloride and subsequent boiling until the original color has again changed to light yellow.

Here, again, since about 1940, the introduction of the ammino nitrite of the metal has offered certain advantages as outlined above for the corresponding platinum salt. By using the same formula as the Pilet one above, but replacing the palladous chloride with the palladium ammino nitrite, the useful life of the bath can be considerably increased, since no chlorides are accumulated during plating operations and the cathode efficiency remains at about 90%. It is important, however, to hold the current density just below the gassing point; otherwise, dark and powdery deposits will result.

The concentration of the salts of the palladium ammino nitrite bath is not critical. The metal content can be increased for making heavier deposits without changing the characteristics of the deposit or the plating conditions. The pH is preferably kept at about 7.0 by adding ammonia from time to time. Deposits obtained at a pH below 7.0 may be slightly brighter but have a tendency to peel.

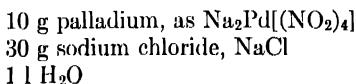
The patent literature since about 1940 lists a great number of palladium bath patents;⁷⁻¹¹ however, upon checking the claims experimentally, it has been found that many of them are inoperative or impractical. Most of the commercially available solutions are supplied in form of concentrated solutions.

During World War II palladium was the only platinum metal available for unrestricted use. For this reason it found extensive application as an ornamental and protective finish. It also was used to some extent, either alone or as an underplate for rhodium, on certain parts of radar or electronic apparatus.

With the rapid developments in the field of ultrahigh frequency applications, the use of palladium has increased steadily until today the metal has assumed a very important place with great possibilities for the future in the electronic industries.

Here the specifications call generally for a thickness of 0.00004 to 0.0002 in., and such deposits can be obtained from some of the solutions described above.

A very suitable plating bath for this particular use is described by R. H. Atkinson and A. R. Raper.¹² Essentially this is a sodium-palladium nitrite bath of the following composition.



If operated at a pH of 4.5 to 6.5, the palladium anodes are soluble with close to 100% efficiency, and the cathode efficiency is about 90 to 95%. Deposits of 0.00004 in. and more are bright when plated at current densities of from 3.8 to 10 amp/sq ft.

Nickel is not a very suitable underplate for palladium owing to a tendency of the palladium to peel. Although palladium can be plated directly on copper and its alloys, a silver flash or plate is desirable.

RHODIUM

Even though a few references to the electrodeposition of rhodium are found in the literature prior to 1915, this metal was never used to any extent for plating purposes until 1930.

The first attempts to plate with rhodium employed the commonly known rhodium salts such as the chloride or the sulfate. Although deposits can be obtained from these solutions, they are far from satisfactory. A rhodium bath made up according to any old Pilet formula using rhodium chloride with a mixture of sodium and ammonium phosphates yielded deposits of steel-blue color and had an extremely poor throwing power. A number of patents^{13,14} have been issued for rhodium plating solutions which cover alkali double nitrites in acid or alkaline solutions, rhodium sulfate or chloride in combination with corresponding alkaline salts, and free acid and rhodium ammino cyanides.

In general, it may be said that only acid electrolytes will give a bright, white deposit and at the same time show good throwing power. The solutions which have been most successful in this country are of the acid type. They comprise rhodium sulfate dissolved in dilute sulfuric or phosphoric acid, or rhodium phosphate in combination with some acids. Although rhodium sulfate is a well-defined compound of the formula $\text{Rh}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, there seem to exist a number of rhodium phosphates of a more or less complex nature to which no definite formulas can as yet be assigned.

Upon attempting to isolate these complex phosphates in salt form, they undergo changes, or decompose, making identification difficult if not impossible. It is only by rigorous and scientific control during rhodium salt manufacture that a constant and uniform product can be obtained. This also explains why rhodium for plating purposes is now sold in the form of concentrated solutions.

The rhodium plating solutions in practical use today, whether rhodium sulfate or rhodium phosphate, usually have a metal concen-

tration of 5 dwt/gal. This concentration is entirely arbitrary and has been adopted as a compromise; it keeps the initial investment and the drag-out losses low and has at the same time enough metal in solution for quick coverage at a reasonable cathode efficiency.

The acid concentration is not very critical and can range from 10 cc/l (1.3 liq oz/gal) upward for either sulfuric acid or phosphoric acid. Higher acid concentration tends to lower the cathode efficiency slightly.

A representative formula for a rhodium plating bath as used today is

RHODIUM PLATING BATHS

1. Sulfuric acid concentrated, c.p.	2.5 liq oz/gal (20 cc/l)
Rhodium metal in prepared concentrated solution	5 dwt/gal (2 g/l)
2. Orthophosphoric acid (85%)	5-6 liq oz/gal (40 cc/l)
Rhodium metal in prepared concentrated solution	5 dwt/gal (2 g/l)

It is important in making up either bath to add the acid to the water before adding the rhodium. If this is not done, the rhodium compound may be partly precipitated by hydrolysis. Even if the precipitate may gradually go into solution again, the bath will not yield white deposits.

The best working temperature is around 40° to 45°C. A current density of 10 to 100 amp/sq ft may be used. Insoluble platinum anodes are employed, and the metal content is replenished by the addition of the concentrated rhodium solution.

A good rhodium solution of this type should produce a bright deposit of approximately 0.00015 cm (0.00006 in.) in 30 min at 20 amp/sq ft which does not require buffing. The throwing power approaches that of a gold or silver cyanide bath.

Figures 1 and 2 are based on tests with a standard rhodium plating bath containing 2.5 to 3 liq oz/gal of concentrated sulfuric acid, c.p., and 5 dwt/gal of rhodium metal in the form of the commercially available complex phosphate. The curves of Fig. 1 show the effects of bath temperature and current density on cathode current efficiency. The curve in Fig. 2 shows the relation between rate of deposition and the metal concentration of the bath.

It has become common practice to use a nickel or bright nickel undercoat for rhodium, except in the case of gold alloys and platinum bases. Zinc, tin, and lead alloys must receive a good, heavy nickel undercoat so as to completely protect the basis metal from the action of the rhodium solution. This holds true whether the rhodium is plated from either the phosphoric acid or the sulfuric acid bath.

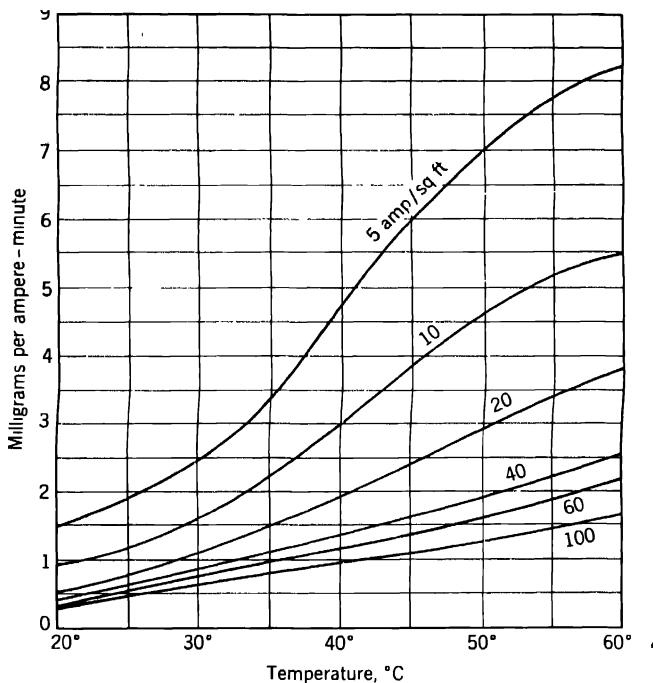


Fig. 1. Effect of bath temperature and cathode current density on current efficiency.

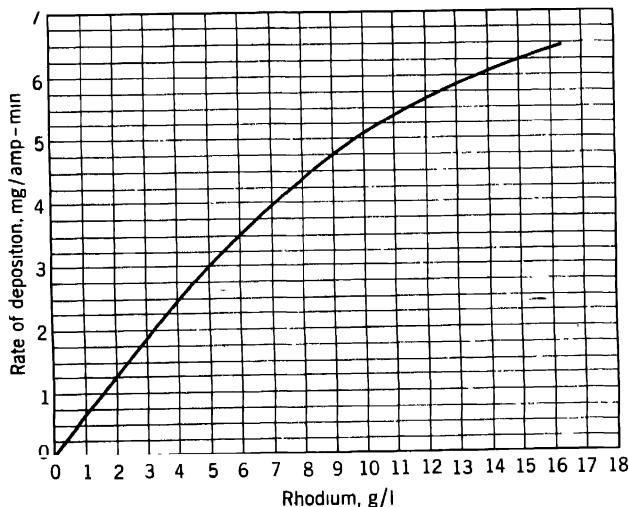


Fig. 2. Effect of rhodium concentration on cathode current efficiency. Bath composition: Sulfuric acid, 4.7 oz/gal; rhodium, 0 to 2.1 oz/gal, temperature, 35°C; current density, 36.2 amp/sq ft.

Heavy rhodium deposits up to 0.0005 in. thick found a limited application during World War II where highest wear and corrosion resistance were required. The following formula is recommended for producing such heavy deposits.

Rhodium metal as rhodium sulfate	1.34-2.7 oz/gal (10-20 g/l)
Concentrated sulfuric acid, c.p.	20 cc/l
Current density	5 amp/sq ft or below
Temperature	50°C (122°F)

Rhodium deposits are characterized by their high reflectivity, the ratio of reflected light to incident light being 78%. The hardness of the plate ranges between nickel and chromium. In most cases rhodium is applied as a flash plate averaging less than 0.000001 in. (0.0000025 cm) in thickness. For silverware and for high grade reflectors for searchlights (some are 1.5 m in diameter) and for motion picture projectors, a plate up to 0.0000075 in. (0.000018 cm) in thickness is recommended.

RUTHENIUM

The following formula has been recommended for a ruthenium bath:

Ruthenium nitroso chloride, RuNOCl,	10 dwt/gal (4 g/l)
Concentrated sulfuric acid, c.p.	2.5-3 liq oz/gal (20 cc/l)
Current density	20 amp/sq ft
Voltage	2.5 v
Color of deposit	Rather dark

ANALYTICAL METHODS

Analytical methods for the exact determination of the platinum metals in plating solution are somewhat complicated, owing to the highly complex nature of the compounds in the bath. Accordingly, highly specialized methods of analysis are employed. As long as the solution is not contaminated with other metals, the platinum metals can be determined by electrolysis, that is, by "complete depositing out," but the results thus obtained will, as a rule, be short of the actual amounts present.

In the case of rhodium solutions, colorimetric methods have been worked out, and a kit containing the necessary materials and apparatus is available. The results thus obtainable are accurate to about 0.1 to 0.2 g/l provided that the plating solution to be tested is not contaminated by other metals.

15.

Silver

N. E. PROMISEL*

Silver coatings are applied to a great variety of basis metals and alloys because of the unique properties that silver exhibits in the decorative, electrical, chemical, and mechanical fields. Its pleasing decorative appearance is the chief reason for its use on tableware, decorative metal objects for the home, and musical instruments. In the electrical field it finds wide usage for electrical and electronic circuit parts because of its high conductivity. The general insolubility of silver in most corrosive mediums makes it useful in the manufacture of chemical engineering equipment and surgical instruments. Silver deposits are used in the mechanical field because of its high load-carrying and non-welding properties under marginal lubrication for the fabrication of bearings, thrust washers and anti-fret surfaces in thicknesses from 0.0005 in. (0.013 cm) to about 0.060 in. (0.15 cm) compared to approximately 0.002 in. (0.052 cm) maximum for most other applications.

Silver finds wide usage on non-metallic materials such as glass and plastics for the manufacture of mirrors and ornamental objects. Finally, it should be mentioned that the electrodeposition of silver in the silver coulometer forms the basis of the international ampere. Other applications exist, but silver plating as discussed in this chapter has to do only with the deposition of smooth, dense, adherent deposits on a metal or alloy basis metal and does not include electroforming, electrorefining, etc.

The origin of silver electrodeposition is closely related to the birth of the electroplating industry. The earliest patent granted for the application of the principles of electrodeposition for decorative purposes is credited to Elkington and Barratt, of England, in 1838. Two years later, Elkington received a patent for silver plating. Oddly enough, this patent describes essentially the present-day silver plating bath, that is, the double cyanide bath with excess alkali cyanide.

* Navy Department, Bureau of Aeronautics, Washington, D. C.

CLASSES OF BATHS (TO 1913)

In the hundred years that have elapsed since the work of Elkington, numerous investigations and publications have dealt with variations of his formula, together with many other novel ones. The literature up to 1913 has been well reviewed by Frary,¹ and the solutions used up to that date may conveniently be divided, for the most part, into the classes shown below.

SIMPLE SILVER SALTS (IN ACID OR AMMONIACAL SOLUTION, WITH AND WITHOUT ADDITION AGENTS)

Thorough investigations of silver nitrate in a nitric acid solution, with and without addition agents such as glue,² have not developed a commercial electroplating bath; the same applies to other silver salts such as the fluosilicate, fluoborate, perchlorate, methyl sulfate, bisulfite, iodide, lactate, citrate, and tartrate. In the non-plating field, the nitrate solution is used industrially for the electrolytic parting of silver from gold and in the standard silver coulometer.

ALKALI CYANIDE SOLUTIONS (PLUS SILVER COMPOUNDS MADE FROM THE NITRATE, CHLORIDE, OXIDE, OR ANY OTHER SILVER COMPOUNDS EXCEPT THE CYANIDE)

Silver chloride in particular was popular, probably because it was so readily prepared, in a relatively pure state, from scrap silver or waste silver solutions. Ferrocyanides were also frequently used as a partial substitute for cyanide itself. Brighteners such as carbon disulfide were used to improve the otherwise dull, milky appearance of the silver deposit. These baths enjoyed some limited commercial success in the decorative field.

FREE ALKALI CYANIDE SOLUTIONS OF SILVER CYANIDE

These solutions are similar to the silver plating bath originally described in 1840. This bath with its carbon disulfide brightener has definitely established itself as superior to all others because of simplicity, stability, ease of operation, favorable electrochemical properties and attractive appearance of deposits, especially in the decorative plating field. However, silver plating for engineering applications has imposed in many cases quality standards on the heavy deposits,

together with numerous anode limitations which required some modifications to this basic bath. The chief modifications are the addition of potassium nitrate and hydroxide, either alone or together.

Current investigations devoted to silver plating are not so much concerned with finding radically new types of solutions, though such work is in progress, as they are with modifying the present cyanide bath in order to: (a) permit the use of higher current densities without sacrificing the appearance of the silver deposits; (b) improve the throwing power so as to secure better distribution of the deposit; (c) control the corrosion of silver anodes; and (d) apply mechanized equipment such as plating machines, automatic filtration, anode and cathode agitation, and more efficient racking methods. It is from these studies that we may expect the future progress in commercial silver plating.

FUNCTIONS OF CONSTITUENTS OF BATH

SILVER CYANIDE COMPLEX

Silver cyanide is by far the most important source of silver ions in cyanide silver plating solutions. Regardless of the manner in which silver enters the plating bath, whether through silver cyanide additions or through the dissolution of silver anodes, its solubility and ion concentration depend upon the presence of sodium or potassium cyanide, which forms with silver a soluble complex anion, predominantly $\text{Ag}(\text{CN})_2^-$. Chemical calculations are therefore based on a ratio of two molecules of the alkali metal cyanide to one atom of silver. The greater the excess of alkali metal cyanide (usually called "free cyanide") above that required to form the anion, $\text{Ag}(\text{CN})_2^-$, the greater the decrease in the concentration of the silver cation. However, the silver cation concentration is essentially independent of small changes in the metal concentration within the usual bath-operating range.

ELECTRICAL RESISTIVITY

The actual electrical resistivity of the silver plating solution is determined by all the bath constituents present and is usually between 5 and 20 ohm/cm³. The numerical values in Table 1 illustrate the relative magnitude of the three common constituents which have the most significant effect on resistivity and all other ingredients within conventional plating range.

TABLE 1. THE EFFECT OF INCREASING CONCENTRATIONS OF ADDED INGREDIENTS ON THE RESISTIVITY OF A CYANIDE SILVER PLATING SOLUTION

Effect of Potassium Carbonate			Effect of Free Sodium Cyanide			Effect of Potassium Nitrate		
Concentration		Resistivity, ohm/cm ³	Concentration		Resistivity, ohm/cm ³	Concentration		Resistivity, ohm/cm ³
oz/gal	g/l		oz/gal	g/l		oz/gal	g/l	
1.9	13.9	9.6	1.0	7.5	14			17.5
10	75	6.2	4	30	11	10	75	9
17.4	130	5.0	6	45	9	16.1	120	6.6

It will be noted in Table 1 that resistivity may be reduced appreciably with small additions of salts when the original value is high. As the resistivity decreases, the amount of added material required to reduce it further becomes comparatively greater. The literature shows no evidence of silver baths having resistivities below approximately 5 ohm/cm³ at room temperatures. This is evidently near the limiting value, and solutions are planned to approach it as closely as other factors demand or allow.

Where resistivity measurements are not feasible, an approximation of this value may be obtained by means of hydrometer readings. Baths having specific gravities above 1.120 (15.5 Bé) will generally have specific resistivities between 5 and 6 ohm/cm³.

FACTORS AFFECTING POLARIZATION

Measurement of cathode polarization in silver solutions is subject to considerable difficulty and is rarely reproducible. A thorough study of this subject is yet to be made, but the known trends are often helpful in analyzing plating conditions.

Free alkali cyanide, besides reducing resistivity and serving as a complex anion builder, increases the cathode polarization, makes possible good corrosion of the anodes at low current densities, and favorably affects the physical properties of the deposit. The alkali carbonate also decreases resistivity, increases cathode and anode polarization, and improves the physical properties of the plate. Increasing the silver concentration decreases cathode polarization and resistivity and has little effect on the physical properties of the plate, provided that the concentration is sufficient for the specific plating conditions.

Of the other ions that occur in silver plating solutions, the two that have received greatest consideration are sodium and potassium, the relative merits of which have long been argued. It has been shown³ that the cathode polarization at which so-called "burned" deposits occur is lesser in sodium cyanide solutions than in potassium cyanide solutions because the potassium bath has greater conductivity. This is the chief reason for the general preference which exists for the potassium cyanide solution, since, in general, a potassium ion bath will permit a 20 to 25% increase in current density over the corresponding sodium ion bath with a whiter deposit. The solubilities of the respective carbonates are also important. Owing to the greatly decreased solubility of sodium carbonate in the silver plating bath at low temperatures,* difficulty is sometimes experienced when a plating solution high in this salt is allowed to cool. At such times, small crystals of sodium carbonate may form and anchor to the cathode itself, causing faulty silver deposition. Another undesirable effect when the carbonate concentration has reached 10 oz/gal is a rise in cathode polarization. This condition frequently results in "burned" deposits which can be minimized by keeping the sodium carbonate below 6 oz/gal, while the concentration of potassium carbonate may safely be permitted to reach 15 oz/gal. Since the latter is approximately the equilibrium value between drag-out in commercial plating and chemical formation from cyanide,† an added advantage for the potassium salt over the sodium salt is evident. The only advantage for the use of sodium salts is the lower cost as compared with potassium.

Experimental studies indicate^{4,5} that chloride, formate, acetate, hydroxide, phosphate, borate, and sulfate ions increase the hardness of the silver deposit as plated, this hardness being lost on heat treatment above 300°C, with borate and chloride ions having the greatest effect. The cathode polarization in all cases was reported to be considerable. It seems likely that the effect of these ions, phosphate, borate, etc., on the physical appearance of the cathode is associated with their influence on a colloidal substance derived from the carbon disulfide or its reaction products.

Carbon disulfide is the primary addition or brightening agent in current commercial use in the decorative field. It is invariably added to the bath as a solution or suspension made by taking a small sample

* This is a universally recognized fact, but numerical values are not available. However, in pure water, sodium carbonate dissolves to the extent of 7.1% at 0°C; and 45.4% at 100°C.

† Carbon dioxide from the atmosphere is absorbed by the bath and reacts to form carbonate: $2\text{NaCN} + \text{CO}_2 + \text{H}_2\text{O} = \text{Na}_2\text{CO}_3 + 2\text{HCN}$.

of the plating bath or a fresh potassium cyanide solution and dissolving the carbon disulfide in it. This addition causes an immediate drop in cathode polarization which is only transient. Although it is possible, using this brightener, to produce nearly mirror bright deposits under ideal conditions, it is more common practice to add only enough of the brightener to produce semi-bright deposits. Such deposits are finished with little more effort than is required for the brightest obtainable, and, even in the latter case, some finishing or buffing operation is usually necessary. On a single cathode of irregular shape such as a teaspoon, it is possible to have many degrees of brightness, varying sometimes in sharply defined bands because of differences in agitation. It is interesting to note that what is essentially a silver plating solution is used for electropolishing,⁶ the major differences being a reduced free cyanide (about 2.5 oz/gal) and an increased current density (about 15 to 25 amp/sq ft).

BATH COMPOSITION

DECORATIVE SILVER

POTASSIUM CYANIDE BATH

The silver plating bath commonly used for most purposes except bearing plating contains:

Silver (as metal)	3-4 troy oz/gal (25-33 g/l)
Free potassium cyanide	4-6 oz/gal (30-45 g/l)
Potassium carbonate	4-12 oz/gal (30-90 g/l)
Carbon disulfide brightener as needed	Up to 0.0001 fl oz/gal (0.9 mg/l)

A concentration of silver higher than 4 oz/gal may be employed where the added cost is compensated for by a higher limiting current density. However, a large increase in silver content of the bath has an adverse effect on its throwing power and, to some extent, on anode polarization. Below 3 oz/gal of silver, a lower current density range becomes necessary; but this is sometimes acceptable where the resulting greater throwing power at such low current densities is required. Furthermore, below 3 oz/gal the silver losses due to drag-out are reduced.

A minimum of 5 oz/gal of free cyanide is usually required to maintain satisfactory anode corrosion. The free cyanide content may be raised appreciably above 5 oz/gal without affecting the appearance of the silver plate; furthermore, throwing power is improved and higher

current densities are permissible under otherwise favorable conditions. On the other hand, under some conditions, a large excess of free cyanide will reduce or completely destroy the effect of the carbon disulfide brightener. A noticeable effect in the behavior of the brightener may be expected at a free cyanide concentration above 8-9 oz/gal.

When a new bath is being made up, potassium carbonate is added to improve conductivity and to increase cathode polarization. Potassium carbonate is the normal decomposition product of potassium cyanide, and its concentration tends to increase on continued operation and aging of the bath.

SODIUM CYANIDE BATH

These solutions are frequently made with sodium cyanide and sodium carbonate where economy prohibits the use of the more expensive potassium salts. The following concentration ranges are typical:

Silver (as metal)	3-4 troy oz/gal (25-33 g/l)
Free sodium cyanide	4-5 oz/gal (30-38 g/l)
Sodium carbonate	5-6 oz/gal (38-45 g/l)
Carbon disulfide brightener	0.0001 fl oz/gal (0.9 mg/l)

The only major difference in desirable range of concentrations between this sodium cyanide solution and the potassium solution specified above is in the carbonate content. The undesirable effects of high concentrations of sodium carbonate have been described above. It may be noted that, by limiting a silver plating solution to this lower total carbonate content, bath conductivity is sacrificed and throwing power is decreased.

MIXED SODIUM POTASSIUM AND NITRATE BATH

The following silver plating solution, attributable to Wood, which is slightly different from the conventional ones, is in limited use today:

Silver (as metal)	2.0 2.3 troy oz/gal (16-18 g/l)
Free sodium cyanide	2-3 oz/gal (15-22 g/l)
Sodium carbonate	max. 3 oz/gal (max. 22 g/l)
Potassium nitrate	15-20 oz/gal (113-150 g/l)

In spite of the lower range of silver concentration, the current density range is equivalent to the higher silver concentration in the conventional bath.

In potassium nitrate-cyanide solutions such as the above, anode corrosion appears to be due in part to the nitrate ion.* This allows a

* Silver may be stripped electrolytically from steel in a solution containing only potassium nitrate and ammonium hydroxide.

lower range of free cyanide concentration as compared to the nitrate-free baths, even in the presence of carbonate, which tends to decrease anode corrosion. In the presence of nitrate, brighter deposits are usually possible. Satisfactory anode corrosion may be had at as little as about 1 oz/gal of free cyanide. Concentrations of free cyanide higher than 3 oz/gal have no adverse effect except where maximum brightness is needed, which is accompanied by a slight improvement in throwing power and covering power.

In principle, a freshly prepared nitrate-cyanide bath contains no carbonate; however, carbonate is formed in the bath, and, at a concentration above about 3 oz/gal, maximum brightness is no longer obtainable. However, up to this value, 3 oz/gal, the carbonate may be considered a tolerable impurity. When maximum brightness is unimportant, the presence of a higher carbonate concentration may be accepted as contributing to higher cathode polarization with improved throwing power.

In the nitrate-cyanide bath, the potassium nitrate has a beneficial effect on the appearance of deposits and on the operation of the bath. On the other hand, when sodium nitrate replaces the potassium salt, a very undesirable plating bath is obtained. It is possible to use a mixed potassium nitrate and sodium cyanide bath provided that the potassium nitrate concentration is kept relatively high with respect to the total sodium salt concentration.

SILVER STRIKE BATHS ON NON-FERROUS BASIS METALS

A "strike" solution is generally necessary to promote adhesion. Sodium salts—not potassium salts—are used universally for these solutions. The most common "strike" solution for basis metals other than steel contains:

Silver (as metal)	0.4–0.6 troy oz/gal (3–4.5 g/l)
Free sodium cyanide	8–12 oz/gal (60–90 g/l)
Sodium carbonate	1–4 oz/gal (8–30 g/l)

Below 0.4 oz/gal of silver, a smutty, burnt deposit on high current density areas may result. At concentrations much above 0.6 oz/gal of silver, the cathode current efficiency improves to such an extent that, for the short period usually involved in a "strike," little or no gassing may occur; the "strike" operation becomes nearly equivalent to that of a regular plating operation, and thus falls short of performing its desired "strike" functions. Large concentrations of free sodium cyanide, 11 oz/gal and higher, cause very low cathode current efficiency, necessitating a longer striking time to obtain adequate or complete

coverage. Concentrations of free cyanide below 8 oz/gal reduce the normally high cathode polarization and high conductivity, and therefore cause poor covering power and throwing power. The sodium carbonate is sometimes added to a new "strike" to improve both factors, but more often the carbonate of the bath results from the decomposition of the cyanide in the bath.

SILVER STRIKE BATH FOR FERROUS BASIS METALS

Steel is now rarely plated directly with silver, but, when it is, a "first strike" is used, such as:

Silver	0.1-0.2 troy oz/gal (3 ₄ -1 ₁ / ₂ g/l)
Free sodium cyanide	8-20 oz/gal (60-150 g/l)

The combined effect of reducing the silver concentration of the first "strike" formula and of increasing the free cyanide is to decrease the silver ion concentration to an extremely low value which insures good adhesion of the deposit on steel. There is evidence⁷ that the strike produces crystal nuclei at edges of ferrite crystals, promoting intraatomic bonding prior to growth of these nuclei in subsequent silver plating.

PREPARATION OF BASIS METALS

There are three problems in silver deposition which require consideration in preparing the basis metal. These are:

1. The possibility of deposition by immersion or replacement, with poor adhesion. Electrical contact before immersion in all silver baths, including strike baths, minimizes this phenomenon.
2. The difficulty of covering solder or other areas on which the deposition potential of silver is greater than on surrounding basis metal.
3. The tendency of the silver deposit, under certain conditions, to reproduce macroscopically the surface structure of the basis metal and thus introduce a finishing problem. In this connection, the cathode polarization is at first lower on a coarse surface, as for example when etched to expose the structure, than on a smooth, polished surface. After some minutes of plating, however, the polarization values on both types of surfaces approach each other.

In some cases, all three problems may be solved by the use of one or more silver "strikes" preceding the plating operation. The strike solution has a lower silver ion concentration than the plating bath, and therefore the tendency to plate by immersion is reduced. The lower cathode efficiency of the strike operation introduces cathodic reduction by hydrogen, which, in turn, promotes good adhesion even

when slight deposition by immersion is known to occur. A higher average cathode polarization voltage is possible in the strike. This is perhaps due to the selective stirring effect of the hydrogen gas bubbles at the high current density areas, which stirring lowers the tendency to burn, at least for the short period involved. If the strike operations result in masking the basis metal influences with a relatively heavy silver deposit applied at high potential, satisfactory deposition may follow in the plating solution. If the strike deposit is not heavy enough or if it, too, has failed to compensate for the basis metal influences, then part of the strike deposit of silver may be found to have dissolved during the subsequent plating operation. Thus, on the otherwise well-plated cathode, the "counterpotential areas" emerge from the bath unplated, or, under the same conditions, a thin silver plate will cover the basis metal but reproduce its surface structure, particularly at the low current density areas.

It is not always possible to obtain satisfactory adhesion and coverage by the use of a silver strike alone. In preparing copper and brass articles for the silver plating bath, a mercury dip often precedes the silver strike and results in improved adhesion. Undercoats of nickel or of tin are also used to minimize deposition of silver by immersion and to mask basis metal influences. Nickel and tin are usually preferable to mercury, especially if it is possible to secure satisfactory coverage at low cathode efficiency; in such cases, cathodic hydrogen, if not excessive, will assist in producing good adhesion of the intermediate deposit of nickel or tin.

OPERATING CONDITIONS AND CHARACTERISTICS

The fairly recent advent of very high current densities in the commercial electroplating of most metals has not been paralleled in the case of silver, where very small gains have been made over older practice. The notable exception has been in the field of silver-plated bearings, which are separately covered later. The exact values of the current densities which continue to be used, predominantly in the range of 5 to 15 amp/sq ft, depend upon whether or not a preliminary silver "strike" is used or whether a silver plating bath is used direct. In either case, the current density depends also on bath composition; on the thickness of silver to be deposited; on the nature of the article; on the geometry of the setup; on the amount and type of agitation employed; and on the temperature of the bath.

A strike solution is always operated at room temperature, and there is always a certain amount of agitation due to the hydrogen gas

liberated at the surface of the article being plated. This agitation is generally augmented, however, by a gentle rocking of the cathode itself. Under such conditions, the current density for the first 5 to 15 sec is in the neighborhood of 25 amp/sq ft, and for articles not having deep recesses and prominent projections this period is often long enough for striking. Where a longer strike is desired, say, for about 1 to 3 min, the current density is dropped to 10 to 15 amp/sq ft, and, where strike solutions are used to deposit a desired thin coating (without any further silver plating), the maximum current is even lower than 15 amp/sq ft. In all cases, lower current density values may be used if the resulting decreased throwing power is acceptable. Special "strike" conditions for silver on steel in the manufacture of electron tubes have been described by Freedman.⁸

In regular silver plating solutions, the range of current density is generally from 5 to 15 amp/sq ft, at about 27°C. When relatively flat objects are to be plated and careful cathode racking is practiced, and if the bath is properly agitated and general optimum conditions are maintained, the lower values can be raised to 15 amp/sq ft and good plate obtained. It should be emphasized that all these current density figures are average ones, obtained by dividing the total current used for several or many objects racked in parallel by the estimated total area being plated.

Higher current density ranges are made possible by using potassium rather than sodium cyanide; by keeping the carbonate concentration (expressed as potassium carbonate) below 10 to 12 oz/gal; by cautiously adding carbon disulfide; by raising the bath temperature; by improving the rack design; and, within narrower limits, by improving the agitation of the bath. The most important factor of all of these is the increase in temperature, and it is often possible to increase the current density by 50% upon increasing the temperature by 11°C. An increase in current density is accompanied by an increase in throwing power; by an increase in anode polarization; by an increase in cathode polarization (unless gassing occurs); and, up to a certain point, by an improved appearance of the silver deposit.

Most silver plating solutions are operated between 24° and 32°C. In fact, there is a strong tendency not to control the temperature, unless it drops much below 24°C, so that the above range usually does hold over both summer and winter. In some cases, a temperature near 35°C may be employed. The higher bath temperatures are sometimes preferred because of possible higher cathode current densities and improved dissolution of the anode. However, the disadvantages of high bath temperatures also become more marked. They are: decreased

brightness of deposit; more rapid loss of carbon disulfide with accompanying increased difficulty in controlling the solution and quality of plate; more rapid loss of cyanide⁹ and thereby increase in carbonate concentration; and, finally, associated with the last, an increase in obnoxious fumes. Consideration of these disadvantages has tended toward general adoption of a temperature range of 27° to 30°C.

Some attempts have been made to include a pH range in the specifications for commercial silver plating. A pH of about 11.5 (colorimetric) has been recommended.¹⁰ Unpublished experiments, however, indicate that there is little to be gained from pH determination in silver plating and that, in fact, some confusion and erroneous deductions may result from its use.

A consideration of current efficiencies, usually necessary for most metals, is unnecessary in the case of silver plating, since under normal operating conditions both cathode and anode efficiencies are essentially 100%. In strike solutions low cathode efficiency is to be expected, but, aside from the problem of holding down the metal content of the solution, this is of little importance. With the plating solution having constant cathode efficiency, throwing power becomes a function of the solution conductivity and rate of change of cathode polarization with current density, a condition relatively simpler than in most plating baths. Compared to other commercial plating baths, the silver solution may be considered to have very good throwing power. At 27°C and at an average current density of 7 amp/sq ft with a cathode distance ratio of 1 to 5 as determined in a Haring and Blum throwing power cell,¹¹ a numerical value of 55% is normal for still silver solutions; and a value of 40% is expected with mild agitation of cathodes.

Owing to very low cathode polarization at which silver plating is usually accomplished, covering power is comparatively poor. Burning occurs at 0.5 to 0.7 v cathode polarization, which means that average cathode polarization is of the order of 0.3 to 0.4 v. On low current density areas, which consequently are areas of low cathode polarization, values of the order of 0.1 v may become evident. Counterpotentials of this magnitude are experienced on multiple cathodes and may result in failure to cover areas where the metal is less noble than that of the balance of the cathode, or on areas having a greater degree of oxidation or strain, such as may be caused by coarse grinding or cold working. The common means of counteracting poor covering power of silver solutions is to insure complete coverage in the strike operation which is performed at higher average cathode polarization. If a heavy strike deposit is used to cover the areas exhibiting counter-

potential, it is usually possible to complete the silver deposit in the plating solution without difficulty.

SPECIAL CONDITIONS FOR HIGH SPEED PLATING OF BEARINGS, ETC.¹²⁻²¹

World War II created an important demand for steel-backed, silver-plated bearings and similar applications. The silver deposit for this purpose was required to be fine-grained and free from excessive nodules, in thicknesses (prior to machining) up to approximately 0.06 in. (0.15 cm). After machining, from 0.004 to 0.040 in. (0.01 em to 0.14 cm), a thin layer of lead-tin or lead-indium is deposited on the silver to improve seizure resistance under marginal lubricating conditions. Of particular importance is the adhesion of the deposit to the steel, which led to a number of tests, including heating to about 538°C (if no copper is used under the silver), dissection, ultrasonic inspection, "hammer and chisel" test, radiography, fluorescent penetrant inspection, vibrating impact tests and others. In general, the high degree of adhesion was obtained by careful degreasing and alkaline cleaning, hydrochloric or sulfuric acid pickling (sometimes anodically), and striking with either nickel or copper prior to a silver strike. There is a real question as to the absolute need for a nickel or copper strike, but its use (particularly the nickel strike) appears to make the process more foolproof. Occasionally a second silver strike, or a low current density silver flash, is used before the main plating. Electrical contact is made prior to immersing the bearing in the silver strike or plating solution. Owing to the heavy coatings required, considerable emphasis has been placed on high current density. The higher plating speeds are made possible primarily by increasing the agitation, raising the temperature, improving the symmetry between anode and cathode, and adjusting the solution composition, particularly the metal content, brightener, and pH. Temperatures have ranged as high as 55°C for using current densities, under selected conditions, upwards of 150 amp/sq ft. More commonly, however, a temperature in the neighborhood of 38° to 47°C is used, with current densities between 75 and 100 amp/sq ft. Special conditions of agitation have been established, which generally require a special setup for each bearing. The latter are used concentric with a circular cast or slotted anode, rotating either the cathode or the anode (usually the former) 100 to 200 rpm, with mild agitation or rapidly circulating the electrolyte past the cathode. An extremely clear solution, preferably constantly filtered, is necessary.

It is not surprising that large variations in solution composition and procedure detail exist. The reader should refer to the many excellent articles¹²⁻²¹ on this subject. For general information, however, the following may be noted. Some of the silver strikes used are not greatly unlike those mentioned previously. The main plating bath often differs significantly. Ranges of the most common ingredients are approximately as follows:

Silver cyanide	6-18 oz/gal (45-135 g/l)
Potassium cyanide (free)	6-20 oz/gal (45-150 g/l)
Potassium carbonate	2-10 oz/gal (15-75 g/l)
Potassium hydroxide	0.5-4 oz/gal, generally intermediate (4-30 g/l)
Brightener	As necessary, with frequent or continuous additions

The brightener commonly used for these high speed baths is ammonium thiosulfate, which is easily controlled. Sometimes this salt is fortified with additional ingredients, notably ammonium polythionates.²¹ Amounts in the order of a few tenths of a gram per liter are generally used.

MAINTENANCE AND CONTROL OF DECORATIVE SILVER BATHS

In silver plating baths, as in other baths, filtration of the bath is resorted to as a specific cure or treatment for rough deposits. Periodic filtration is a common preventive measure, with intervals varying from six months in some plants to one month in others. Where frequent filtration is practiced, it is usually directed toward removal of particles of colloidal dimension or close to it. For this purpose, a filter aid, generally diatomaceous earth, is used. This type of filtration is based on, and supports, the theory that carbon disulfide brightener produces a solid colloid phase in solution. When brightness of plate falls off in spite of the usual brightener additions, and under otherwise normal conditions, filtration with diatomite is resorted to, in order to remove the agglomerated solid colloid product. By this procedure the normal colloidal phase is likewise removed, as is indicated by the fact that a plating solution producing bright deposits ceases to do so after diatomite filtration. Furthermore, the plating solution again performs normally, producing acceptable bright plate, upon addition of fresh quantities of carbon disulfide after diatomite filtration. Continuous filtration, coupled with continuous brightener addition, appears to be a logical and desirable procedure. That this is not in general use may

be due to the difficulty of avoiding introduction of air into the bath during filtration. Air has a distinctly undesirable effect in tending to produce pitting of the silver deposit. Furthermore, filtration must necessarily be thorough and rapid for, if not, stirring up residual particles during filtration will usually give rise to rough silver deposits. Filtering through activated carbon has been observed to "remove certain cumulative impurities not removed by other filtering processes" but cannot be said to be in general use.

In most plants the presence of impurities is no serious problem in silver plating, as it is in nickel plating. Although little is known of the effect of foreign metals on silver plate, no difficulties are traced to any, with the possible exception of iron. This metal may reach a high concentration in the plating bath and has been observed to cause a yellowish tint in the silver deposit.

No method has been reported for removing impurities by electrolysis of the silver solution. Low temperature is commonly applied to the bath to reduce the sodium carbonate concentration in sodium cyanide baths. At the same time, the iron concentration can be lowered by crystallization and removal of the iron as the ferrocyanide. Owing to its higher solubility at low temperature, potassium carbonate is not amenable to the same treatment as sodium carbonate. However, potassium carbonate is rarely objectionable in low current density plating and usually levels off around 13 oz/gal. In the potassium nitrate-cyanide solution, the carbonate is readily removed by precipitation with calcium nitrate.

In silver plating practice today, the maintenance and control of the baths are based primarily on chemical analyses and on the appearance of the deposit. The former determines the maintenance and control of the concentration of silver, free cyanide, carbonate, and metallic impurities. Physical appearance of the plate determines the addition of carbon disulfide, which is normally the only other bath ingredient considered. The optimum concentration of carbon disulfide is not quantitatively known, nor can it be controlled by quantitative analytical means. This difficulty would appear to be due to the fact that carbon disulfide itself is not the direct brightening agent.²² It is important, however, to avoid excess brightener because of its deleterious effects on the deposit.

The only other tests occasionally made on silver plating solutions are the determination of cathode and anode polarization. These tests are usually made in a Haring cell¹¹ at the usual operating temperature and range of current density. Such tests, however, are not of the

routine type, but are rather special, being of assistance in determining the cause of occasional plating results which are unsatisfactory without apparent cause. As general criteria in these tests, maximum figures of about 0.2 v for anode polarization and about 0.5 v for cathode polarization are normal. If values found are unusually high, an attempt is made to correlate them with excessive carbonate in solution, or with low free cyanide or with other analytical data.

In silver plating solutions the normal tendency toward stratification is particularly objectionable. Continuous or daily stirring is common to limit the effect of this phenomenon.

ANALYTICAL METHODS

The United States Bureau of Standards' Research Paper 384 adequately covers methods of analysis for free cyanide, silver, and carbonate. The methods described in this paper are as follows:

FREE CYANIDE

To a 20-ml sample of the plating solution, add 0.1 g of potassium iodide (or 0.2 g for badly contaminated solutions). Dilute to 250 ml and titrate with 0.1 *N* silver nitrate solution. The endpoint of the titration is the first appearance of opalescence, best observed with a black background.

$$1 \text{ ml } 0.1 \text{ } N \text{ AgNO}_3 \approx 0.00980 \text{ g NaCN or } 0.01302 \text{ g KCN}$$

SILVER

Treat 10 ml of plating solution with 20 ml of concentrated sulfuric acid. Evaporate to fumes of sulfur trioxide in a well-ventilated hood. Add a few drops of concentrated nitric acid, if necessary, to hasten decomposition of organic matter, and again evaporate to fumes; cool, dilute to 150 ml, and warm until all solids are dissolved. Add 3 ml of saturated ferric ammonium alum solution and titrate with 0.1 *N* potassium thiocyanate to the appearance of a pink coloration.

$$1 \text{ ml } 0.1 \text{ } N \text{ KCNS } \approx 0.01079 \text{ g Ag}$$

CARBONATE

To the solution resulting from the Liebig titration for free cyanide add a few drops of phenolphthalein solution and titrate with 0.5 *N* hydrochloric acid until the pink color is completely discharged.

$$1 \text{ ml } 0.5 \text{ } N \text{ HCl } \approx 0.0530 \text{ g Na}_2\text{CO}_3 \text{ or } 0.0691 \text{ g K}_2\text{CO}_3$$

ANODES

Silver is very easily soluble anodically in solutions containing any appreciable concentration of cyanide ions. Except in a few cases to be mentioned below, pure silver anodes are almost universally used in silver plating. Their dissolution at practically 100% current efficiency under normal operating conditions makes the replenishment of silver in the bath by this method ideal, for the cathode current efficiency (also 100%) is thereby counterbalanced. The slight chemical attack of the silver anodes tends to replace that additional amount of silver lost by drag-out. The exceptions are: the use of insoluble anodes (steel) in the deposition of silver purely for the reclamation of the metal; and the use of insoluble anodes together with silver anodes in some silver strike solutions, where, owing to the low cathode current efficiency, the silver content of the bath will increase excessively if silver anodes alone are used. The satisfactory insoluble anodes include low carbon steel, platinum, carbon, and stainless steel if used at low anode current densities, the choice depending upon the particular application.

The silver anodes should be 999.5+ fine for best results and minimum trouble with "black anodes." The almost universal anode shape or form is the rolled silver strip, cut to the consumer's specified sizes. The general practice today is to give the silver strip a final high temperature anneal after rolling. Before a new anode is suspended in the plating tank, it is, in some plants, surface cleaned. However, as a rule this is not necessary.

The 0.05% impurities in the silver anodes, which are the major cause of "black anodes," are described in the literature as chiefly lead,²³ iron, bismuth, manganese, tellurium, selenium, sulfur, and antimony. A premium grade of anode silver 999.9 fine in some cases is superior to the lower purity grades for plating, but it is rarely necessary in commercial installations.

A contributory cause of "black anodes" is improper solution composition. The desirability of having a relatively high concentration of free cyanide has been mentioned. The formation of "black anodes" can be caused by a high iron content in the plating solution. The literature²³ attributes the formation of "black anodes" to the presence of sulfide and thiocyanate in the bath.

In general, bagging of the anodes should be used wherever feasible to minimize anode sludge from getting into the bath.

ANODE CURRENT DENSITY

Modern low current density practice in silver plating is to use an anode current density rarely exceeding 10 amp/sq ft. This corresponds roughly to a ratio of anode to cathode area of not less than 1:1. The addition of sodium or potassium cyanide reduces this polarization voltage as does the removal of carbonate from solution. The presence of carbon disulfide in the bath has little effect on anodic polarization. Considerably higher current densities in bearing plating, in many cases as high as 500 amp/sq ft, are made possible by the addition of nitrate and hydroxide anions without producing "black anodes."

TESTS OF DEPOSITS

Probably because of the intrinsic value of silver metal, "specification plating" was commonplace in silver plating long before plating standards were adopted in the plating industry as a whole.

FLATWARE

Flatware is generally silver plated on a basis equivalent to so many troy ounces of silver per gross of teaspoons. The usual weights of silver on spoons are:

Federal specification plate	280 g or 9 troy oz/gross of teaspoons
Quadruple	250 g or 8 troy oz/gross of teaspoons
Triple plate	187 g or 6 troy oz/gross of teaspoons
Double plate	124 g or 4 troy oz/gross of teaspoons
Standard plate	62 g or 2 troy oz/gross of teaspoons
Half-plate	31 g or 1 troy oz/gross of teaspoons

Other items of flatware are plated with weights of silver in the same ratio to that of the teaspoon as the ratio of surface areas. So-called "fancy" or serving pieces are sometimes plated at lower weights than are accompanying "staple" pieces, in view of the lighter use expected.

Additional "spot-plates" or overlays are sometimes applied at one or more points of maximum wear, 47 g or 1½ troy oz/gross being the greatest weight, known to the author, to be added in this form.

CUTLERY

Cutlery is plated on a basis equivalent to so many pennyweights of silver per dozen solid-handle dinner knives, plated all over. The usual weights for cutlery are:

Hotel plate	31.1 g or 20 dwt/doz dinner knives
Federal specification plate	26.4 g or 17 dwt/doz dinner knives
Heavy plate	24.9 g or 16 dwt/doz dinner knives
Standard plate	18.7 g or 12 dwt/doz dinner knives

As in the case of flatware, smaller knives, and those on which only the handle is plated, are plated with weights in proportion to the area and silver weight for dinner knives.

HOLLOW WARE

Hollow ware silver plating is not so well standardized as are flatware plating and cutlery plating. A Federal specification exists,²⁴ and hotel hollow ware is handled with fair uniformity by the larger manufacturers, but the commercial grades, including such items as tea sets, sandwich plates, trays, candy dishes, lack even the nomenclature of standardization, except by the individual manufacturer. The following values indicate the weights generally employed for hollow ware:

Federal specification plate	20 dwt/sq ft (33.5 mg/sq cm)
Extra-heavy hotel plate	15 dwt/sq ft (25.1 mg/sq cm)
Heavy plate	10 dwt/sq ft (16.8 mg/sq cm)
Medium plate	6 dwt/sq ft (8.4 mg/sq cm)
Light plate	2 dwt/sq ft (3.4 mg/sq cm)

A deposit of silver weighing 20 dwt/sq ft (33.5 mg/sq cm) has an average thickness of about 0.00125 in. (0.032 mm). This thickness is the basis for the Federal specification shown above, from which other thicknesses may be estimated.

THICKNESS

Because thickness of a silver deposit is most commonly specified in terms of weight, tests for thickness are usually made by stripping the entire deposit. The piece is weighed before and after stripping, and the surface area determined to allow calculating the pennyweights of silver per square foot (or milligrams per square centimeter). In the case of silver-plated steel or Britannia metal, the deposit is stripped anodically in sodium cyanide solution. From nickel-silver, brass, or copper, the silver is dissolved in a mixture of 19 parts of concentrated sulfuric acid to 1 part of concentrated nitric acid at a temperature of 80°C.

When a direct thickness measurement is required, the Mesle chord method^{25, 26} is used; or the determination is made by preparing a cross section of the plated article for observation and measurement under

the microscope. On steel, the magnetic method²⁷ is applicable. The "jet" test, as described by Hammond,²⁸ favorably compares²⁹ in accuracy with the microscope method and is more readily accomplished.

PHYSICAL PROPERTIES

Deposits are rarely tested for physical properties except by the practical criticism of their finishability. A deposit which can be readily brought to a high luster by buffing is considered a good deposit, and conversely a deposit which requires undue effort in finishing is poor.

16.

Tin

Tin is useful for its resistance to corrosion and tarnish, for its non-toxic nature, and for its solderability, softness, and ductility; it owes most of its uses as a coating to one or more of these characteristics. As a coating on steel it is more noble than the basis metal and therefore does not offer sacrificial protection; but this situation is usually reversed under the conditions obtaining inside a hermetically sealed "tin can." The metal itself is quite tarnish-resistant, and if deposits were thick enough to be substantially non-porous they would be corrosion-resistant.

In the past most tin coatings were produced by hot-dipping, but electroplating has been gradually displacing the hot dip method since about 1930. The largest single use of tin coatings is in the tin plate industry: in this field electroplating had made no inroads at all until about 1942, but ten years later more than 65% of all tin plate made in the United States was electrotinned.

The electrolytic method has gained its present preference over hot-dipping for a number of reasons, among which are:

1. The development of satisfactory baths, both acid and alkaline. Early tin plating solutions were not competitive with hot dipping because they gave unsatisfactory deposits, were unstable, or both; but modern baths leave little to be desired in either respect.

2. There are substantially no domestic sources of tin; thus U. S. Government restrictions on its use have been in almost continuous effect since the beginning of World War II.* Much thinner deposits can be produced electrolytically than by hot-dipping, and if the thinner coating will do the job it will result in economies in tin consumption. This factor, coupled with developments by the can industry which rendered the thinner coatings practically usable, is one of the major reasons for the phenomenal growth of the electrolytic tin plate industry.

3. Electroplating is often more economical than hot-dipping for reasons other than those discussed above. Coatings can be made more uniform, and no dross is formed.

* These restrictions were removed while the book was in press.

4. Heavy coatings can be produced more satisfactorily by the electrolytic method. There is no actual upper limit to the thickness of coatings obtainable by electroplating; plates as thick as 0.005 in. or more are easily produced.

5. Oddly shaped, recessed parts which are hardly susceptible to hot tinning at all can be successfully electroplated.

6. Electroplating can be applied to some basis metals which cannot be hot-tinned, such as zinc and aluminum.

In addition to its use in the tin plate industry, tin is employed as a coating on refrigerator evaporators, dairy and other food-handling equipment, washing machine parts, builders' hardware, radio and electronic components, electrical lugs and connectors, copper wire, and piston rings. Tin coatings on copper wire protect the wire from the sulfur in the insulation as well as provide solderability; and electro-tinning is beginning to compete with hot-dipping in this field also. Another important use of electro-tin deposits is for bearing surfaces. Although tin itself is not one of the best bearing metals, it can be used for this purpose in a large number of cases and has the advantage of being easily applied. In this connection may be mentioned the tinning of automotive pistons for breaking-in purposes: the tin may be applied by aqueous immersion (on aluminum alloy) or by electro-plating (on cast iron). Here the tin acting as a bearing surface prevents seizing and scoring of the cylinder walls.

In addition to the foregoing applications, there is of course a large list of miscellaneous uses of tin coatings. Whether to consider tin as a coating in any particular application will depend on the balance between its relatively high cost and lack of sacrificial protection on the one hand, and its non-toxicity, ease of application, solderability, softness and ductility, and tarnish resistance on the other.

Electroplated tin coatings of appreciable thickness, from either acid or alkaline solutions, are not "bright." They can in many cases be brightened after plating by melting the tin coating, an operation often called "reflowing," which produces a finish practically indistinguishable from hot-dip. All electrolytic tin plate is thus reflowed as are some other plated articles. Although many methods (including induction, resistance, and radiant heating) of bringing the coating to the required temperature just over the melting point of tin (232°C) are used in continuous strip processes like electrolytic tin plate manufacture, only one has been found practical for general plating: the use of hot oil or fat. The oil is generally a long chain fatty acid ester of glycerin such as palm oil, tallow, or partially hydrogenated oils from various sources. The oil should have a sufficiently high flash point for the temperature required, and some free fatty acid to act as a flux;

and the reflowing should be carried out as soon as possible after plating. For successful reflowing the tin coating should be neither too thick nor too thin; too thin a coating will not come out bright, and too thick a plate will tend to de-wet or gather up into beads. Average limits for successful brightening by this method are 0.00005 to 0.0003 in., although the size and shape of the work, nature of the basis metal, and other factors may modify these limits. Large flat areas have more tendency to de-wet than wires and rounded shapes. It should also be mentioned that the successful reflowing of tin deposits depends on a good plating job; unsound deposits that might "get by" if left in the as-plated condition will not reflow properly.

Tin plating baths are of two general types, the alkaline stannate and the acid; each type is treated separately in the discussions which follow. The authors present the principal arguments in favor of their respective subjects; it need only be added that the acid baths have found greatest favor in applications where high deposition rate and economy in power cost are paramount, while the stannate solutions are the choice in general job plating and wherever the greatest degree of throwing power and ease of operation are attractive. Both types of solutions, as well as all specific examples of each type, have their advantages and disadvantages: there is no one "best" tin plating bath.

In addition to electroplating and hot-dipping, tin can be applied to many metals by immersion processes requiring no current. Such methods have their special applications and are considered separately later in the chapter. Finally, the electroplating of tin alloys has within the past few years received much attention, especially through the work of the Tin Research Institute of England, and a separate discussion is devoted to this subject.

STANNATE TIN

FRED BAUCH * AND F. F. OPLINGER †

HISTORICAL DATA

Methods for the electrodeposition of tin from either acid sulfate or alkaline solutions have been known for many years. Morewood and

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Rogers,^{1,*} 1843, are among the earliest tin platers. In 1850 Roseleur² was granted a patent for depositing tin from solutions containing tin crystals ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and sodium pyrophosphate. In 1871 De Lohstein³ obtained a patent on a solution containing caustic soda, potassium cyanide, and tin crystals. Two years later Fearn⁴ was granted a British patent on a solution prepared from tartaric acid, potassium hydroxide, and fused stannous chloride.

The 1893 edition of the Langbein-Brannt book⁵ gave a number of formulas and references having to do mainly with baths made up from stannous chloride and potassium hydroxide. Sometimes small amounts of potassium cyanide were added. Stannous ammonium chloride was added at other times. Very little progress was made for thirty years. The 1924 edition of the Langbein-Brannt book quotes almost the same formulas, except that in one case a more highly concentrated solution was recommended for operation at high temperature.

The whole subject of the electrodeposition of tin was reviewed by Kern.⁶ Mathers and Cockrum⁷ published results on the effect of various addition agents and later tested solutions mentioned by Kern. They concluded that alkaline baths were difficult to operate and offered few commercial possibilities. Most of the bath formulas recommended in the early references had little or no value for commercial purposes. Often the baths were uneconomical, the anodes failed to dissolve, large amounts of sludge were formed, and, as a rule, the baths were short lived owing to the formation of spongy deposits (except in the case of flash coatings). Alkaline baths in particular were unsatisfactory on this account.

No progress of any importance in alkaline tin plating was made until about 1921, when sodium stannate was introduced to the plating trade. Before this, the little alkaline tin plating that was done was carried out in solutions prepared from stannous chloride and caustic soda or potash with, frequently, an addition agent.

Mathers and Bell⁸ showed that satisfactory deposits could not be obtained from the following bath: stannous chloride, 8 oz/gal; caustic soda, 8 oz/gal; addition agent, 0.13 oz/gal, because of the oxidation of sodium stannite which could not be prevented; nor could the stannate formed be reduced back to stannite. As was pointed out by Foerster,⁹ most investigators failed to recognize that strongly alkaline solutions of sodium stannite revert to stannate and sponge tin spontaneously. This accounts for the early failures to obtain consistent results with the alkaline tin baths. Furthermore, no one recognized that the pres-

* References for this portion of the chapter will be found on pages 409 and 410.

ence of small amounts of stannite in the stannate bath was very harmful.

Proctor¹⁰ and Fraine¹¹ recommended the following bath: sodium stannate, 28 oz/gal; hydrated tin oxide, 2 oz/gal; potassium resinate, 0.25 oz/gal; powdered white starch, 0.13 oz/gal; bath temperature, 70° to 80°C. This bath, with modifications, was used commercially on a large scale; however, the lack of knowledge of anode reactions left much to be desired. Spongy deposits were frequently formed, and the precipitation of insoluble tin salts made the bath expensive to operate. Throwing power was sometimes very poor; it was generally improved by the addition of small amounts of stannous chloride, which also reduced the caustic soda content. Anode polarization was sometimes corrected through the use of steel anodes, which also frequently corrected the formation of spongy deposits, although the reason was not known at that time. Today, we believe it is the oxygen given off at the steel anodes that oxidizes stannite to stannate, thereby eliminating spongy deposits. Nevertheless, commercially satisfactory results were obtained with the Proctor-Fraine bath, and credit must be given to Maeder for having pioneered in operating the first large-sized alkaline stannate solution under mass production conditions.

The major expansion of tin plating from the stannate bath was realized when Wernlund and Oplinger^{12,13} discovered that spongy tin deposits could be prevented by using a low concentration solution of caustic soda and stannate with sodium acetate and hydrogen peroxide. Smooth, white tin deposits of substantial thicknesses could thus be produced from baths varying in sodium stannate content from about 7 to 20 oz/gal, provided that the caustic soda was kept sufficiently low, 0.5 to 2 oz/gal, and the anode current density and temperature were properly controlled. It was shown that the important improvement was the use of a high enough anode current density, together with a low enough free alkali content, so that the anodes filmed over with a greenish yellow film during operation. When this takes place, the anodes remain "clean" and all the tin is dissolved as stannate. This important effect occurs at as low as 5 amp/sq ft if the caustic soda is very low, or at 10 to 40 amp/sq ft, when the caustic soda is raised to about 1 to 2 oz/gal in a solution containing 10 to 20 oz/gal of sodium stannate.

The modern alkaline stannate bath, the development of which has been briefly traced, suffers from none of the serious defects of its predecessors. Once the basic principles of its operation have been mastered, it is a remarkably easy bath to control and maintain and is

particularly outstanding in its tolerance for impurities and its operability over a wide range of compositions and operating conditions. Except for the unusual anode reactions, nothing about the bath is critical, and, although there are of course optimum conditions, the bath will still operate even though many of these conditions are not met. No addition agents of any kind are required. The excellent throwing power of the alkaline stannate bath has become virtually a criterion of performance in the plating industry.

The principal limitation of the sodium stannate plus hydroxide system has been its lack of good cathode efficiency at high current densities; i.e., the relatively slow rate of electrotinning in this solution.¹¹ Operation at higher current densities, in the attempt to increase the speed of tin deposition, is not successful because of the rapid drop in cathode efficiency.¹¹ Many bath compositions have been investigated without appreciably increasing the useful current density range.¹⁵

Another limitation is the relatively low solubility of sodium stannate, lowered further by the presence of sodium hydroxide and by the decrease in the solubility of sodium stannate with a rise in temperature of the bath. Sternfels and Lowenheim^{16,17} recognized that potassium stannate is more soluble than sodium stannate and that the solubility increases with an increase in temperature of the solution. They have shown that, in the presence of 1 mole of alkali per liter (5.3 oz/gal sodium hydroxide or 7.5 oz/gal potassium hydroxide) at 90°C, the sodium solution can contain 13.3 oz/gal of tin, while the potassium solution can contain 45.4 oz/gal. Thus the potassium system offers a wider range of useful compositions, and many of the limitations of the sodium stannate bath are overcome.

The following discussion will of necessity consist of two separate parts: one dealing with the conventional sodium stannate plus sodium hydroxide system, and the other dealing with the potassium stannate plus potassium hydroxide system.

THE SODIUM STANNATE BATH .

The sodium stannate baths are used for depositing tin on many types of small articles, as well as on large equipment, with thicknesses of deposit ranging mainly from 0.0001 to 0.003 in. The principal advantage of this bath is that its application is almost unlimited so far as size and shape of article and type of basis metal are concerned. Another major advantage is its practicability. Once the basic principles are understood, the bath can easily be operated without diffi-

culty. When specification plating is required, means of control are readily available from a number of sources.

The main disadvantage of the sodium stannate bath is the slow rate of deposition due to low cathode current efficiency. Generally, the cathode efficiency in still plating at 15 to 30 amp/sq ft does not exceed 60 to 90%, based on stannic tin. Rates of tin deposition in barrel plating are slower than for deposition of other metals, such as copper or cadmium, from cyanide solution.

Another, but minor, difficulty encountered with the sodium stannate bath is the tendency toward the formation of insoluble tin salts. This results from hydrolysis and absorption of carbon dioxide from the air whenever the alkalinity of the bath is too low. Insoluble tin salts may also form when hard water is used. When available, soft, distilled or de-ionized water should be used to maintain bath levels, and the caustic content should be kept high enough so that carbon dioxide absorption from the air does not cause undue precipitation of insoluble tin salts. Bright, lustrous tin deposits have not yet been produced from alkaline baths.

FUNCTIONS OF CONSTITUENTS OF BATH

SODIUM STANNATE, $\text{Na}_2\text{Sn}(\text{OH})_6$

The sodium stannate is the reservoir for tin which is deposited at the cathode. Maximum cathode current efficiency is obtained only when the tin concentration is 6.0 to 8.0 oz/gal, corresponding to sodium stannate concentration of 15.0 to 20 oz/gal. The sodium stannate of commerce is manufactured from scrap tin plate. Normally, the tin content of the commercial salt is 40 to 42% (theoretical is 44.5%).

SODIUM HYDROXIDE, NaOH

Sodium hydroxide not only improves conductivity but is absolutely necessary to obtain balanced anode corrosion. With too little caustic soda the tin anodes become coated with a film that interferes with proper anode dissolution. In consequence, the tin in the bath soon becomes depleted. On the other hand, an excess of caustic soda must be avoided because it increases the critical anode current density. It also tends to repress the hydrolysis of the stannate and to accept atmospheric carbon dioxide, which would otherwise decompose the stannate. Careful control of the caustic soda content is imperative (1.0 to 3.0 oz/gal).

SODIUM ACETATE

The function of sodium acetate was formerly considered quite similar to that of boric acid in a nickel plating solution; but later investigation showed that it is not necessary, and satisfactory results are obtained without it.¹⁸

HYDROGEN PEROXIDE

This oxidizing agent is added in small amounts, when necessary, to oxidize any stannite formed when the anode current density has been too low. Stannite in appreciable amounts causes spongy and unsatisfactory deposits.

ADDITION AGENTS

As a rule, they are not used. *Sodium resinate* in small amounts appears to have some value as a foaming agent. A small amount of foam on the top of the bath is valuable in preventing contamination of the surrounding atmosphere with spray from the electrodes.

Sodium oleate may also be used as a foaming agent.

Sodium carbonate. During operation of the bath, sodium carbonate is formed through the absorption of carbon dioxide from the air. The effect of sodium carbonate in sodium stannate baths has been studied. No detrimental effects on anode and cathode efficiencies were detected, and the throwing power of the bath improved somewhat in its presence. No sodium carbonate, however, is actually added to the bath.

OPERATING CONDITIONS AND CHARACTERISTICS**CURRENT DENSITY RANGE**

As will be shown in a separate paragraph, the initial anode current density must be equal to or greater than the critical anode current density. The operating current density range is fairly wide, but it is limited by the anode and cathode efficiency balance and by the minimum and maximum current densities. Below the minimum current density, the anode dissolves as stannite, which is undesirable. Above the maximum current density, the anode becomes coated with a black insoluble film. The optimum current density varies with the composition and temperature of the solution. For average operating conditions the anode current density is between 10 and 40 amp/sq ft.

The cathode current density range is very wide, but the cathode efficiency drops rapidly with a high cathode current density. The optimum cathode current density range is between 10 and 25 amp/sq ft.

Very little is gained by using current densities higher than 60 amp/sq ft because the cathode efficiency drops rapidly.

THE TEMPERATURE RANGE

To obtain a high cathode current efficiency and a smooth, sound deposit, elevated temperatures are desirable. The optimum temperature range is between 60° and 80°C.

THE FREE CAUSTIC RANGE

The concentration range for free caustic is also fairly wide, but for practical purposes the range is between 1.5 and 3.0 oz/gal of sodium hydroxide.

CURRENT EFFICIENCIES, THROWING POWER, AND COVERING POWER

The anode current efficiency varies with the composition of the plating bath, the temperature, and the current density. For average operating conditions, it will be between 60 and 90% (on the basis of quadrivalent tin). The anode efficiency increases with the free caustic content.

The cathode current efficiency is affected by the same factors as the anode efficiency and in a similar manner, except that an increase in free caustic lowers the cathode efficiency. It will be between 60 and 90% (as quadrivalent tin) for average conditions.

The throwing power of the sodium stannate solutions is excellent. It decreases somewhat with increase in current density and improves with increase in concentration of metal, free caustic, and sodium carbonate.

CONDUCTIVITY AND POLARIZATION

These factors will vary for each solution, and no coordinated data are available. As a rule, a 6-v source of current is satisfactory for still plating, as the potential drop across the plating bath is normally approximately 4 v. Barrel plating normally requires a 12-v current source.

SOLUTION COMPOSITION

For a conventional bath, compositions are as follows:

	For Still Plating		For Barrel Plating	
	oz/gal	g/l	oz/gal	g/l
Tin	6.0-8.0	45.0-60.0	6.0-10.0	45.0-75.0
Caustic Soda, NaOH	1.5-3.0	11.0-22.0	2.0-4.0	15.0-30.0

MAINTENANCE AND CONTROL

FILTRATION

Filtration of tin plating solutions is quite difficult, but generally unnecessary.

PURIFICATION

By Settling and Decantation. The insoluble sludge which is formed in the stannate tin bath during its operation settles rapidly to the bottom of the tank and causes no harmful effects unless the solution is agitated. Occasional decantation into another tank, removing sludge and pumping the clear solution back into the cleaned tank is the most common and satisfactory method.

PHYSICAL CONTROL OF THE BATH

Very useful information for the control of the tin plating solution is readily obtainable, especially when operating large plating machines. Plating tests are used to determine and check critical current density, anode and cathode efficiency, current distribution, and throwing power. The actual plating solution is used in a small suitable container at specified anode and cathode current densities, and the appearance and quality of tin plate obtained are noted.

ANALYTICAL METHODS

Tin Concentration (Stannate Content). Volumetric Method. Suitable methods are based on the reduction of stannic to stannous chloride, followed by titration with standard iodine solution. Iodate has been found by many workers to be better than iodine as it is more stable.

Reagents required: (a) Standard potassium iodate solution (approximately 0.1 N). For each liter of 0.1 N solution required dissolve 3.6 g of potassium iodate in 200 ml of water containing 1 g of sodium hydroxide and 10 g of potassium iodide. When solution is complete, dilute to 1 liter.

(b) Starch solution (10 g/l). For each 100 ml of starch solution required, make a paste of 1 g of soluble starch in about 5 ml of water and add this to 100 ml of boiling water. Boil for about 5 min or until the solution is clear. Cool before using, and prepare fresh every day.

* In many cases recovery of the tin values in the sludge by sale to a smelter should be considered.

(c) Nickel coil. Roll into a loose coil a piece of nickel sheet 6 by 3 by 0.015 in. Before using the first time, clean in petroleum ether and hydrochloric acid. Thereafter, clean in hydrochloric acid each time before using.

To standardize the potassium iodate solution, place three samples of pure tin, each weighing 0.20 to 0.25 g, in 500-ml Erlenmeyer flasks and add 75 ml of hydrochloric acid and 3 drops of antimony chloride (1%) to each. Upon complete solution of the tin, add 250 ml of water and a nickel coil. Stopper the flask with a one-hole rubber stopper fitted with a $\frac{1}{4}$ -in. glass tube outlet which is bent to be immersed later into a beaker containing a saturated solution of sodium bicarbonate. The sodium bicarbonate should be dissolved in hot water in order that the resulting decomposition can displace with carbon dioxide any air present in the water. Place the stoppered flask on the hot plate and boil gently for 1 hr. Immerse the outlet tube in the sodium bicarbonate solution, taking care that no air is allowed to enter, place the flask in a cooling tank, and allow it to cool to room temperature or lower. Remove the stopper, quickly add a few pieces of granular marble or dry ice and 5 ml of starch solution and titrate with the solution to be standardized.

Sampling. The volume of sample to be taken depends on the approximate concentration of the solution. For a solution analyzing about 12 to 13 oz/gal of potassium or sodium stannate (approximately 5 oz/gal of tin) and about 2.5 oz/gal of free potassium hydroxide, 100 ml of sample are taken. If the tin is 10 oz/gal (or about 25 oz/gal potassium or sodium stannate), 50 ml of sample are taken, etc.

The sample is pipetted into a 500-ml volumetric flask and made up to the mark. Aliquots are taken for the various determinations.

Determination of tin. Transfer a 25-ml aliquot to a 500-ml Erlenmeyer flask, add 75 ml of hydrochloric acid, and dilute to about 300 ml. Place a coil of nickel in the flask, and stopper it with a one-hole rubber stopper fitted with a glass tube outlet $\frac{1}{4}$ by 6 in. Place the flask on the hot plate and boil gently for 1 hr; then place it in a cooling tank, connect it with a "CO₂ apparatus," and cool to room temperature. The "CO₂ apparatus" consists simply of a saturated solution of sodium bicarbonate, which is connected to the flask so that the bicarbonate solution is sucked into the flask as the solution cools, and carbon dioxide is generated in situ. When the solution has cooled, remove the stopper and add a few small pieces of marble quickly; add a few milliliters of starch solution and titrate the solution with standard iodine or potassium iodate which has been standardized against pure tin.

Calculations. S = Tin equivalent of standard potassium iodate solution, in grams per milliliter; T = milliliters of standard solution used in titration. Then, if a 100-ml sample is taken,

$$\text{oz/gal tin} = ST \times 26.7$$

If a 50-ml sample is taken,

$$\begin{aligned}\text{oz/gal tin} &= ST \times 53.4 \\ \text{oz/gal potassium stannate} &= \text{oz/gal tin} \times 2.51 \\ \text{oz/gal sodium stannate} &= \text{oz/gal tin} \times 2.40\end{aligned}$$

For routine analysis the reduction with sodium hypophosphite¹⁰ is very suitable, especially in the modified form of procedure (see below). It involves reduction with sodium hypophosphite in hydrochloric acid solution in the presence of mercuric chloride as catalyst. The reduction and titration are carried out in an inert atmosphere of carbon dioxide.

Reagents required: (a) sodium hypophosphite, 5 g for each test sample; (b) hydrochloric acid, 50 ml concentrated hydrochloric acid + 50 ml water; (c) mercuric chloride, saturated solution; (d) citric acid, 50 g to 100 ml water; (e) potassium iodide, 4% solution; (f) starch indicator; (g) standard iodine solution, 0.1 *N*.

The modified method to avoid external supply of carbon dioxide follows:

Apparatus. A 500-ml flask fitted with a one-hole stopper carrying a glass tube drawn out to a jet at its outer end.

Method. To a 5-ml sample of plating solution add 20 ml of hydrochloric acid and a solution of 5 g of hypophosphite dissolved in 80 ml hydrochloric acid; then add 1 ml of mercuric chloride. Boil gently for 10 min, and add 10 ml of potassium iodide solution, 50 ml citric acid, and 1 ml starch solutions. Then drop two small pieces of marble into the flask, replace the stopper with glass tube, and cool quickly under the tap. When cool, remove the glass tube, insert burette, and titrate.

To prevent appreciable oxidation, it is necessary to avoid violent agitation during cooling and titrating. Results agree within 1 g/l, the modified method giving results 0.5 g/l too low.

Calculation. 1 ml of 0.1 *N* iodine = 0.00593 g of tin = 1.19 g/l on a 5-ml sample.

Gravimetric Method. The following gravimetric method is fast and simple: Take a 10-ml sample of plating solution and add a few milliliters of concentrated nitric acid. Evaporate to dryness on a hot plate, add water and filter while hot, then wash the stannic acid thor-

oughly with hot water. Dry, ignite, and heat to dull red heat, then weigh the residue as stannic oxide (SnO_2). The weight of stannic oxide \times 0.7876 = weight of metallic tin in the 10-ml sample.

Free Caustic Soda Concentration. Reagents required: (a) 0.1 *N* hydrochloric acid solution; (b) 10% barium chloride solution; (c) 1% alcoholic solution of thymolphthalein indicator.

Method. To a 5-ml sample, add 25 ml distilled water and 50 ml of the barium chloride solution. Shake thoroughly, allow to stand for 15 min, add a few drops of the indicator, and titrate with vigorous shaking until the blue color is starting to be discharged. Add another drop of the indicator, and continue the titration. The endpoint is taken when the color changes from a definite blue to practically white. The endpoint is comparatively sharp unless large amounts of sodium carbonate are present. Accuracy within 1 g/l on a 5-ml sample is easily obtainable.

Calculation. 1 ml of 0.1 *N* hydrochloric acid = 0.004 g caustic soda in the 5-ml sample.

Another method for the determination of free caustic soda is to dilute a 5-ml sample, after 50 ml of the barium chloride solution has been added, to exactly 100 ml. Shake thoroughly, allow to settle, and pipette an aliquot for titration.

Sodium Carbonate. Determination of this constituent is hardly ever necessary, except as a matter of information and record. Standard methods based on the evolution of carbon dioxide may be used for this test. Hepburn's²⁰ method has been found satisfactory. If no acetate is present, carbonate can be determined by difference. Determine the total alkali by direct titration; free alkali and tin as earlier described.

Calculation. Total alkali - 0.674 \times tin - free alkali = alkali as carbonate.

Bivalent Tin (Stannite Content). This determination has very little practical value because the stannite content of the solution changes rapidly.

Reagents needed: 20% hydrochloric acid solution; 0.1 *N* iodine solution.

Method. Acidify a 25-ml sample of plating bath and titrate directly with the standard iodine solution.

Calculation. 1 ml of 0.1 *N* iodine solution = 0.00593 g of tin = 0.2372 g/l (on 25-ml sample).

Although, as stated, the quantitative estimation of stannite is of questionable value, a qualitative test for its presence is often useful.

A suspension of bismuth hydroxide is prepared by dissolving 5 g of bismuth oxide or carbonate in 100 ml of 25% hydrochloric acid. The solution is made just alkaline with sodium hydroxide and diluted to 250 ml. To make the test, pour about 5 ml of the suspension (well shaken) through a 9-cm filter paper, and then pour 10 ml of the hot plating solution through the paper. If the precipitate on the paper does not darken, stannite is absent; blackening of the precipitate indicates the presence of major amounts of stannite, while a slight gray color shows that traces are present. Test papers, embodying the principles of this test, are available.

MISCELLANEOUS NOTES ON CONTROL

1. If present in excessive amounts, oxidizing agents tend to lower the cathode efficiency of the stannate bath. These agents should be added to the solution in diluted form.
2. Chlorides are not harmful unless present in large amounts (over 6.5 oz/gal). Then they cause a slow breakdown of the oxide film on the tin anodes. Chloride may also cause corrosion of the tank if it becomes anodic.
3. Frequency of chemical control tests. (a) Free caustic soda; daily. (b) Sodium stannate; once a week at first, then once a month (make periodic additions between tests). (c) Sodium carbonate; once in 3 months or less frequently, depending upon conditions.
4. Sometimes solutions are operated with insufficient ventilation. In such cases, the evolution of hydrogen causes spray which may become very objectionable to persons working in the vicinity. Small quantities of sodium oleate or other soluble soap may prevent this condition.
5. It would presumably be of some advantage to have the plating tank lined with a non-conducting material to eliminate the possibility of the tank acting as anode or intermediate electrode, as well as the possibility of galvanic cell action which would produce stannite. Since, however, very few lining materials are suitable, most installations use unlined steel tanks.
6. Organic addition agents are used occasionally but must be added with caution. Since they do not disperse readily throughout the bath, they may cause a patchy appearance of the deposits. There is also a tendency toward reduced cathode efficiency.
7. Losses due to drag-out may be reduced considerably by a still rinse tank following the plating. This solution is used for replenishing the water of the plating bath.

8. On continuous plating machines, better results are obtained if the load is constant. If the plating tank is not fully loaded, dummy cathodes of steel should be used on carriers to take up the missing load. These dummy cathodes become coated with tin and may be used later as anodes and thus depleted.

9. The contacts between the anode bars and the anodes should be as perfect as possible. Connection by merely hanging on a hook is not satisfactory, unless the bars and the anode hooks are kept scrupulously clean. The anode hooks should be tightly threaded or soldered to assure adequate contacts. Poor contacts on the anodes will cause stannite to be formed in the bath, resulting in unsatisfactory deposits.

ANODES

TYPES

Generally anodes are of pure tin (but see p. 406 and Ref. 28). It is also possible to use insoluble anodes of steel or nickel or other metals heavily nickel plated. In these cases, the tin metal content of the bath can be replenished by anodic regeneration in a separate tank in order to prevent the gradual decrease in tin and gradual increase in free caustic.²¹ The metal content may also be maintained by stannate additions, in conjunction with sufficient acetic acid to neutralize the free caustic formed as the tin deposits.

ANODE CORROSION CHARACTERISTICS

Tin can dissolve in the sodium stannate bath in either the bivalent (stannite) or quadrivalent (stannate) form. As stannite ions cause bulky, rough, and porous deposits, it is important that the anode dissolve to form the stannate. Starting with a low potential across the bath, the current density will increase as the potential is increased until a certain value is reached. At low current density, the anode dissolves as stannite and becomes gray in appearance. When the potential and, hence, the anode current density are increased beyond a certain value, the voltage drop across the bath will suddenly increase without a corresponding increase in current density. This is the critical current density, and the sudden increase in potential may be used as an indication that the critical current density has been reached. The tin then dissolves in the stannate form, and the anode becomes coated with the desired greenish yellow film. If the current is again raised above a certain value, an excessive amount of oxygen is given off at the anode

and little or no tin is dissolved. The anode surface first becomes brown, and later is covered with a highly insoluble black oxide film which is objectionable and is difficult to remove, except with strong mineral acids. After the critical current density has been reached, the current may be lowered in a short time to the normal operating current density, in order to increase the anode efficiency so that the continuous dissolution of tin as stannate is assured. The critical current density is not fixed, but varies directly with the free caustic content and the temperature of the bath; it also increases slightly with the stannate concentration, but is lowered by the presence of sodium carbonate. For a complete discussion, see Ref. 22.

ANIONS ADDED TO INDUCE CORROSION

The hydroxyl anion is needed to induce anode corrosion, and its concentration is maintained by proper control of the free hydroxide content.

PREPARATION OF BASIS METALS

For satisfactory tin deposits the surface should be cleaned and prepared as for any other electrodeposit. No special treatments are needed in preparing the articles to be tin plated.

TESTS OF DEPOSITS

POROSITY

Coatings of 0.00075 in. are considered satisfactory for a non-porous covering on steel. For cast iron, considerably thicker coatings are needed, and 0.001 in. is considered a minimum. Lighter coatings are satisfactory on brass, bronze, or copper. Usually, tin coatings between 0.0003 and 0.0005 in. are substantially non-porous. The porosity is a function not only of the thickness of the plate, but also of the constitution and cleanliness of the basis metal surface, of the correctness of the plating bath, and of the bath temperature and current density used.

ACCELERATED CORROSION TESTS

Porosity Test for Tinned Steel. Both the hot water test and the ferricyanide paper test²³ are used.

The hot water test consists in immersing the carefully degreased tin-plated article in hot distilled water at a temperature between 95° and 100°C. At the end of 6 hr of immersion, adherent rust spots will appear at any pores or discontinuities in the plated surface.

In the ferricyanide paper test a piece of filter paper saturated with ferricyanide solution is placed against the tin-plated surface, establishing as close a contact as possible by means of a soft brush dampened with the reagent. Since the paper will tend to become dry, it should be brushed into place at intervals and kept moist. The dark blue spots that appear at defective points in the tin plate are best observed with a low power lens after a ruled glass sheet has been superimposed over the paper, after it has been removed from the plated specimen.

Porosity Test for Tin on Brass, Copper, or Bronze. In the ammonia fume test, the tin-plated specimen is placed on an inclined and cooled shelf in a closed box at room or elevated temperatures. On the bottom of this box is an open container with ammonium hydroxide. The ammonia fumes will attack the basis metal through any pores or discontinuities in the plate. The specimen is considered non-porous when no dark spots appear on the plate after approximately 4 hr of exposure.

Humidity Test. This test may also be used, but it is too slow for practical purposes.

Salt Spray Test. This is the conventional test used for other deposits, such as zinc on steel.

THICKNESS TEST

Most conventional thickness tests are also applicable to tin deposits, with certain reservations due to the softness of the metal.

A simple drop-test method for tin deposits on brass, copper, or bronze, using dilute (approx. 3 N) nitric acid solution, has been developed by the Manufacturing Research Laboratory of the Frigidaire Division of General Motors. Since the values vary with the various tin plating solutions and methods used, it is best to calibrate this drop test by microscopic or chemical evaluation. Results of the drop test also vary with the temperature of the sample and with the test solution used.

An instrument involving deplating of the specimen, with automatic endpoint indication, is available.*

PHYSICAL CHARACTERISTICS

The sodium stannate solutions give matte-white, smooth, well-adherent, and dense deposits. The microstructure varies with the temperature and cathode current density. The Brinell hardness, measured with a 5-mm diameter ball and 25 kg weight, is between 8 and 9.

* Kocour Co., Chicago, Ill.

THE POTASSIUM STANNATE BATH *

The potassium stannate bath does not have some of the limitations of the sodium stannate bath. Sternfels and Lowenheim^{16,17} showed that potassium solutions are more stable, especially at higher temperatures. This has been verified in commercial application in strip steel electrotinning lines, where less than 1% of tin was found to have precipitated as sludge in a 20,000-gal solution over a 2-month period of operation.²⁴

Since the potassium ion has a higher mobility than the sodium ion,²⁵ potassium stannate solutions have also a greater conductivity than their sodium counterparts. An extensive investigation showed that potassium baths were 25% more conductive than their stoichiometric sodium equivalents.^{16,17} This bath produces as well as the sodium stannate bath. Deposits of good quality are obtainable over a wide range of conditions. But the potassium bath has the same weakness as the sodium stannate bath in respect to formation of stannite if the anode current density is not properly controlled. This tendency may be aggravated by higher temperatures, if proper safeguards are neglected. With excessive current densities, it also may be difficult to maintain the proper anode-to-cathode-area ratio so the bath will remain in a good operating balance without excessive additions of chemicals. A recent improvement in anode composition is claimed to obviate this difficulty.²⁶

FUNCTION OF CONSTITUENTS OF THE BATH

POTASSIUM STANNATE, $K_2Sn(OH)_6$

Potassium stannate is the reservoir for the tin that is deposited at the cathode. The higher the tin content of the solution (free alkali remaining constant), the higher is the current density compatible with good cathode efficiency. (See Figs. 1 and 2.) This effect is one of the principal keys to the superior cathode performance of the potassium bath. Potassium stannate is rhombohedral and is isomorphous with sodium stannate.²⁶ Its properties and preparation are discussed by Zocher.²⁷

POTASSIUM HYDROXIDE, KOH

Potassium hydroxide has the same function as caustic soda in the sodium stannate bath. Its careful control is imperative, as it affects

* Most of the information concerning the potassium stannate bath is based on the papers by Sternfels and Lowenheim.¹⁶

the anode behavior and is necessary for proper anode corrosion. In order to maintain a high cathode efficiency, free potash must be as low as compatible with needed anode efficiency.

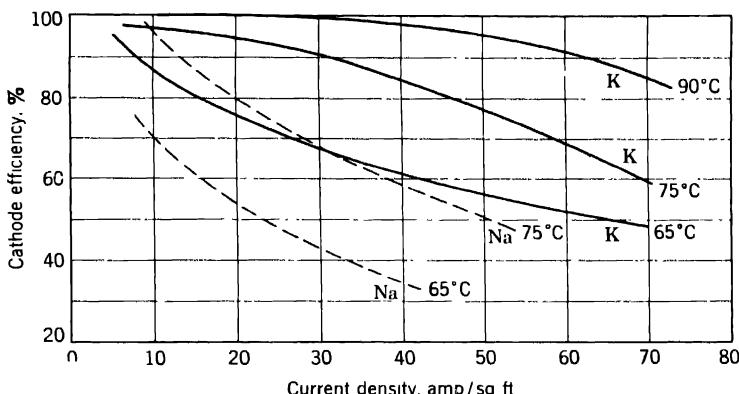


Fig. 1. Cathode efficiencies of potassium and sodium stannate baths of conventional concentration. Bath composition: tin, 5.5 oz/gal; free sodium hydroxide, 1.25 oz/gal, or free potassium hydroxide, 1.75 oz/gal.

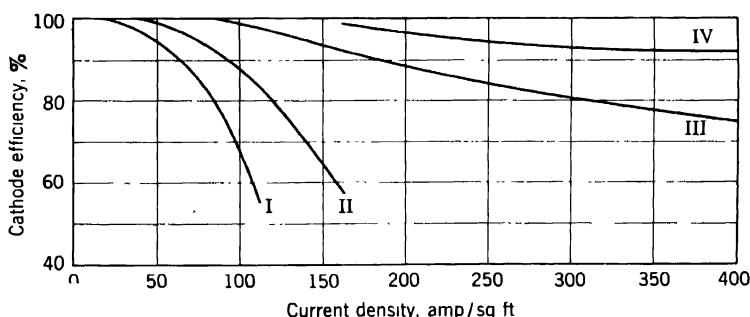


Fig. 2. Effect of tin content on cathode efficiency of potassium stannate baths at 90°C. Tin content: curve I, 5.5 oz/gal; curve II, 10.6 oz/gal; curve III, 21.2 oz/gal; curve IV, 38.7 oz/gal; free potassium hydroxide, 2 to 4 oz/gal.

HYDROGEN PEROXIDE

Hydrogen peroxide serves the same purpose as in the sodium stannate bath, i.e., to oxidize any stannite formed occasionally when the anode current density has been too low.

POTASSIUM CARBONATE

Carbonate is formed during operation of the bath; its effect on anode and cathode efficiency has been found to be negligible within the range of the test (1.34 to 15 oz/gal potassium carbonate).

OPERATING CONDITIONS AND CHARACTERISTICS

CURRENT DENSITY RANGE

Anode Current Density Range. The same considerations apply here as for the sodium stannate bath. For average conditions the current density is between 40 and 80 amp/sq ft. This is a relatively low current density if the cathode current density is high. With higher current densities the anode efficiency is much lower than the cathode efficiency, and it would be difficult in some cases to provide sufficient anode area to operate the bath without excessive additions.

Another consideration is the critical current density initially required to "film" the anode. If the anode area is too great, the initial current surge will require a current supply many times larger than the current used for operation of the solution. An alloy anode has recently been introduced which claims to obviate most of these difficulties and to bring the anode efficiency more nearly into line with the cathode efficiency.²⁸

The critical anode current density increases with an increase in free alkali of the bath in a similar manner to that for sodium stannate solutions, and it also increases with the temperature. An increase in stannate concentration lowers the critical current density somewhat. When the free alkali is only 1.34 oz/gal, this tendency is reversed and the critical current density increases with the stannate content.

No specific data are available in regard to the effect of carbonate, but tests have shown it has virtually no effect upon the operating characteristics of the bath.

Cathode Current Density Range. This range is exceedingly wide, and high current efficiencies are obtainable even at a current density up to 800 amp/sq ft (see Figs. 1 and 2 for cathode current density ranges under various conditions and bath compositions).

THE TEMPERATURE RANGE

To obtain high anode and cathode efficiencies elevated temperatures are essential. The optimum is 90°C.

THE FREE ALKALI RANGE

The free alkali range is also fairly wide, but for practical purposes it should be held between 2 and 6.7 oz/gal.

CURRENT EFFICIENCIES, THROWING POWER, AND COVERING POWER

Anode Current Efficiency. This varies with the composition of the bath and its temperature and with the current density used. The sub-

Substitution of potassium for sodium does not show the improvement in anode current efficiency comparable with that apparent at the cathode. For this reason the anode area must be sufficiently large to keep the current density as low as possible.

Anode efficiency increases slightly with increased tin concentration.

Cathode Current Efficiency. Although this efficiency is affected by the same factors and in a similar manner, an increase in free potassium hydroxide lowers the cathode efficiency.

At 90°C an efficiency of 80% or better may be obtained at a cathode current density of 800 amp/sq ft when the tin content is very high. Even at 70°C the cathode efficiency does not fall to 80% until a density of 180 amp/sq ft is reached. This certainly represents a new phenomenon in alkaline tin plating.

Throwing Power. Throwing power is claimed to be good and comparable to that of the sodium stannate bath.

CONDUCTIVITY AND POLARIZATION

These vary with the composition of the bath, but the conductivity of the potassium bath is about 25% higher than that of a similar sodium bath.

SOLUTION COMPOSITION

The composition of the potassium bath may vary greatly, depending on the desired characteristics. No attempt will be made to note any specific formula.

The tin content may vary between 5.3 and 45.4 oz/gal, and the free potassium hydroxide between 2.0 and 19.0 oz/gal, depending on the characteristics desired. In this manner, it is possible to select a composition suitable for nearly any requirement. Most practical installations operate in the range 6 to 20 oz/gal tin and 1 to 4 oz/gal free potassium hydroxide; operation outside these ranges is found only in special cases.

MAINTENANCE AND CONTROL

The same methods may be used as for the sodium stannate baths, the necessary corrections being applied where needed to obtain correct values for the potassium bath. Sodium stannate discussions on anodes, on preparation of basis metals, and on tests of deposits also apply to potassium stannate solutions.

When potassium is substituted for sodium in stoichiometrically equivalent quantities in a stannate plating solution, the following effects are observed:

The conductivity increases by about 25%, the cathode efficiency is notably raised at higher current densities and the anode current efficiency decreases slightly but irregularly.

The higher solubility of potassium stannate permits baths with higher free alkali to be operated at temperatures unattainable with corresponding sodium stannate baths (see Fig. 3). This results in higher

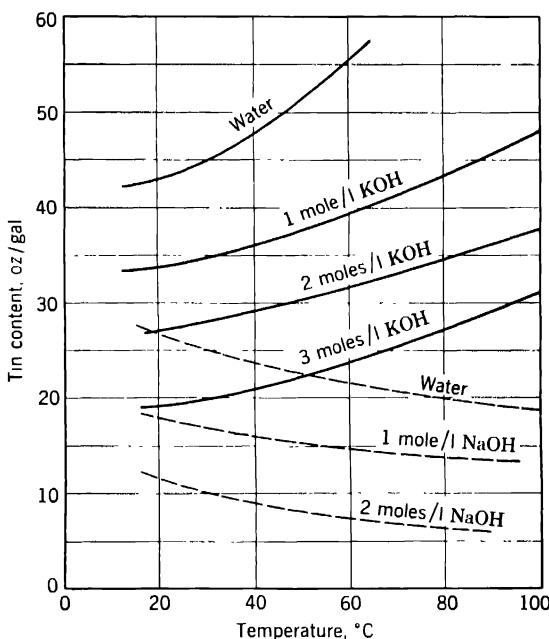


Fig. 3. Solubilities of potassium and sodium stannates in water and alkali solutions.

conductivity and cathode current efficiency as well as increased anode efficiency due to the increase in temperature.

It is evident from the solubility curves of Fig. 3 that a new region of bath compositions exists for the potassium stannate-hydroxide solutions. Investigation showed that variations in bath composition and operating conditions have the following effect upon the plating characteristics of the bath:

1. Increasing free alkali content raises the conductivity markedly and in general decreases the cathode current efficiency, but raises the anode efficiency and the critical anode current density.
2. Increasing the tin content of the potassium stannate bath decreases the conductivity and raises the cathode efficiency. The critical

aliquot current density decreases with increase in stannate, but increases in a bath with very low free alkali content.

All the plating variables under consideration are increased with an increase in temperature.

From data available,^{16, 17} the potassium stannate plus potassium hydroxide system is mainly of advantage for baths with higher efficiencies at current densities considered excessive for the conventional sodium stannate-sodium hydroxide bath.

For this reason the potassium stannate plus potassium hydroxide system is particularly applicable to processes where high plating speeds are desirable, such as steel strip plating and automatic machines; it has also been found advantageous in many classes of barrel work in ordinary job shop plating procedure. Its high-speed characteristics have been utilized to good advantage in a process for continuous plating of copper wire.²⁰ The choice between sodium and potassium is often a close one, and it depends on individual circumstances.

Both the sodium stannate and the potassium stannate systems have a definite field of application.

ACID TIN

PAUL R. PINE* AND A. H. DU ROSE*

The commercial development of the acid tin bath started shortly before World War I and expanded rapidly during the war and shortly after, owing to a demand for a method of obtaining pure metal from Bolivian tin ore.

In 1909 a patent was granted to Hollis^{1,†} which covered a solution which may be considered the forerunner of the modern acid tin bath.

* Harshaw Chemical Co., Cleveland, Ohio.

† References for this portion of the chapter will be found on pages 427 and 428

Hollis' solution was an adaptation of the Betts lead process, introduced in 1902, to the electrorefining of tin. It was a fluosilicic acid bath with additions of glue or gelatin to give smooth deposits.

In 1914 Mathers and Cockrum² investigated several acid baths. Of the chloride, fluoride, perchlorate, and fluoborate, the fluoborate in conjunction with clove oil gave the best deposits. In 1915 and 1916 two patents were granted^{3, 4} for the electrolytic refining of tin contaminated by lead; the process consisted of adding free sulfuric acid to Hollis' solution to precipitate the dissolved lead and thus prevent its deposition. Whithead⁵ in 1915 also recommended a bath containing 6% tin, 15 to 20% fluosilicic acid, and 0.1% sulfuric acid. Mathers and Cockrum⁶ in 1916 were unable to obtain good deposits from mineral acid solutions, but realized that an addition agent might be found which would make possible a smooth deposit. In 1918 Kern⁷ suggested the use of aloin or peptone in the fluosilicate bath.

When sulfuric acid is used in the fluosilicate bath, excessive amounts cause loose, non-adherent deposits to form. In 1921 Mathers⁸ patented the use of cresylic acid in a bath containing sulfuric acid. This had the effect of allowing the presence of a higher concentration of sulfuric acid without the detrimental effect of producing tree-like deposits, and also allowed for the use of less tin in the solution. A suggested solution composition is Sn 2%, H₂SO₄ 5%, H₂SiF₆ 5.5%, cresylic acid 0.3%. This valuable contribution was followed by a slightly different type of bath when Schlötter⁹ was granted patents covering a bath containing stannous chloride, hydrochloric acid, gelatin, and phenol. In 1922 a bath containing potassium fluoride, hydrofluoric acid, and stannous fluoride was patented by Schulte.¹⁰ Licorice root, molasses, and glue were mentioned as addition agents. Some trouble had evidently been encountered with anode polarization at higher anode current densities, for in 1924 a patent was granted¹¹ covering the use of halogen compounds in the acid bath to aid in anode corrosion.

After World War I the trend of electrorefining of tin was turning rapidly toward the use of less fluosilicate, largely as a result of investigations of Fink,¹² Stack,¹³ and Alexander.¹⁴ By 1923, when electrorefining of tin practically ceased in the United States, the fluosilicate had been entirely eliminated. An average composition at this time consisted of 4 oz/gal of tin, 11 oz/gal of sulfuric acid, 5 oz/gal of cresol sulfonic acid with frequent additions of glue and cresol¹⁵ during electrolysis.

Attention now turned from refining of tin and production of heavy deposits to producing deposits for corrosion resistance or appearance.

In 1923 two patents were issued, to Simpkins¹⁶ and to Fink,¹⁷ pertaining to addition agents and salts for the sulfate bath. Simpkins' patent covered the use of β -naphthol along with a colloid, and Fink's covered several colloidal or near-colloidal substances, such as aloin and tannic acid, and the use of sulfates of magnesium, iron, titanium, and aluminum. It was claimed that these sulfates improved the anode corrosion. In 1925 Mathers¹⁷ disclosed what was in effect an application to electroplating of his work on electrorefining; the bath contained stannous sulfate, sulfuric acid, cresylic acid, and glue.

In the 1930's several patents were issued to Schlötter¹⁸ in which a number of addition agents were mentioned, such as sulfonates, phenols, higher alcohols, and one bath containing tin naphthalene-tetrasulfonate and water. In 1935 Pine¹⁹ patented addition agents prepared by condensing cresol with gluc, aloin, and aldehydes. Instead of using glue or gelatin, Campbell²⁰ proposed sulfuric-acid-treated wool in conjunction with cresol or its sulfonate. In 1937 Nachtmann²¹ patented a method for plating continuous strip basis metal, suggesting several addition agents for use in the sulfate bath, like sulfonates and hydroxy acids such as succinic acid. A British patent²² was issued in 1938 in which addition agents such as mono-, di-, and triphenols, aminophenols, anthrol, anthranol, phenanthrol, and hydroxy anthraquinone are mentioned.

Hothersall and Bradshaw²³ have described procedures using various combinations of addition agents including cresolsulfonic acid, β -naphthol, lysalbic acid (from egg albumen), resorcinol, and *p*-isooamylphenol. In more recent years patents have been issued covering new addition agents for the acid tin bath such as pyroligneous acid,²⁴ alcohol sulfates²⁵ as wetting agents, sulfones of phenols,^{26,27} *o*-cyclohexylphenol, *o*-phenylphenol and nicotine,²⁸ dispersed phenolic resins,²⁹ sulfoxides as bis-(*p*-hydroxyphenyl)sulfoxide,³⁰ dihydroxy-diphenyl sulfone, monobutylphenyl phenol sulfonate, diphenyl-*p*-phenyl diamine.³¹ Mathers and Discher³² give results using sorghum, Tergitol-4, Guinea Green, and β -hydroxyethyl-*m*-toluidine.

In addition to the sulfate bath, recent literature and patents have discussed the fluoroborate baths,³³⁻³⁶ stannic chloride solutions,³⁷⁻³⁹ and oxalate solutions.⁴⁰⁻⁴² The complex oxalate bath seems to be limited by a low permissible current density.

Probably the largest single advancement in recent years has been the du Pont "Halogen" tin process,⁴³⁻⁴⁵ which has made possible extremely rapid deposition of tin on strip steel. We may expect to a certain extent the continued and expanding use of fluoroborate solu-

tions for tin and tin alloys. Solder has been made commercially for a number of years by codeposition.¹⁶ The fluoborate solutions permit higher tin concentrations and higher current densities than the sulfate bath.

PRINCIPLES

Of all the types of tin baths proposed there are only three which are now widely used. These are referred to as the alkaline stannate bath, the acid bath, and the "Halogen" bath. The acid radical of the acid bath may be either sulfate or fluoborate, and the general principles which follow refer to both of these modifications. Organic addition agents are required in the acid bath, but this should not be considered a disadvantage if the addition agents are controllable as to composition, performance, and concentration. The ultimate use of the deposit should be considered since some addition agents cause deposits which are difficult to flow-brighten and solder.¹⁷

Although the acid baths are inferior to the alkaline with respect to throwing power, they are very good when compared with many other acid electrolytes. Acid tin baths are much more economical of power than the stannate baths: their electrochemical equivalent of tin is double, the cathode efficiency usually higher, and the voltage appreciably lower. All these factors combine so that in favorable cases the power yield of the acid solution may be as much as 10 times as high as of the stannate. Speed of plating in the acid electrolyte is also usually superior to that in the alkaline.

THE SULFATE SOLUTION

FUNCTIONS OF CONSTITUENTS OF THE BATH

Stannous sulfate is used almost universally to furnish the metal ions in the acid sulfate bath. In the United States the stannous sulfate is generally added as such, but in Great Britain the tin is often introduced by "anodic dissolution of tin in sulfuric acid solution, the cathodes being enclosed in porous pots."¹⁸

Sulfuric acid and frequently alkali metal sulfates and sulfonates are used to obtain better conductivity. These also have another function; the common ion effect suppresses the tin ion concentration—a common device in electroplating. By suppressing the tin ion concentration, there is less tendency to produce tree-like deposits and a smoother deposit results.

ADDITION AGENTS

Without addition agents the acid tin bath could not be used. The commercial application might be said to depend as much on the addition agent as on the tin in solution. Without addition agents the de-

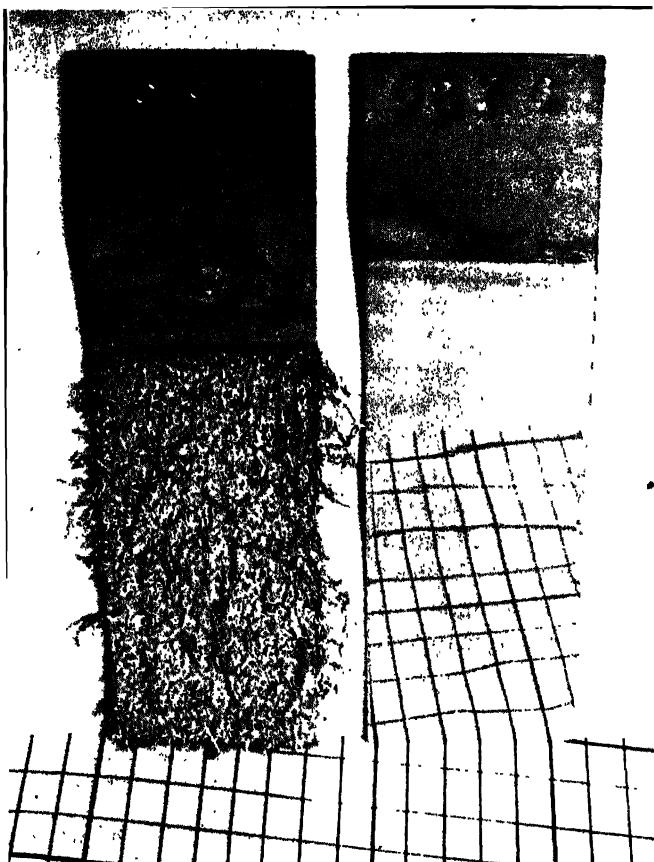


Fig. 1. Effect of addition agent in acid tin plating. Left, from bath with no addition agent; right, from bath with addition agent.

posit is loose, crystalline, and tree-like (Fig. 1). The addition agent also has a tremendous effect on the throwing and covering power as shown in Table 1. From the theoretical standpoint there has been little of importance published on tin addition agents. Loshkarev and associates⁴⁹ studied the effect of some compounds on the limiting current density, and Lainer⁵⁰ the effect on cathode polarization.

Although there is some overlapping, compounds which when added to the acid bath cause smooth, matte, and sometimes bright deposits may be divided into the following classes:

1. Colloids of low gold number or high protective value, such as glue, gelatin, and lysalbic acid.

2. Ring compounds containing a hydroxyl group and relatively insoluble side chains. The most common examples are cresol and naphthol, although the ring does not necessarily have to be aromatic since terpineol, isoborneol, and cyclohexanol are effective. In cyclohexanol the additional hydrogens act as side chains. Although α - and β -naphthol are effective, a dihydroxy naphthalene with one hydroxyl group on each ring is relatively without effect. Likewise, 3-4-dihydroxy biphenyl is effective but symmetrical dihydroxy biphenyl is not. The phenols without side chains, such as phenol and resorcinol, are relatively ineffective.

3. Secondary and tertiary amines such as diphenylamine and dibutyl aniline. These represent an interesting class since the results, with a few exceptions, correlate very well with Mann's⁵¹ theory of inhibitor action. For instance, dibutylamine is much more effective than primary octyl- or dodecylamine and 2-biphenylamine is much more effective than 4-biphenylamine.

4. Non-ionic high molecular weight compounds containing ether linkages⁴³⁻⁴⁵ and certain ethoxy fats and amides.

5. Sulfoxides such as dihydroxy diphenyl sulfoxides⁵⁰ and phenoxyanthin monoxide. The sulfones seem to be relatively ineffective compared to sulfoxides.

Examples of overlapping between these classes are ethoxyamines (classes 3 and 4) and diethyl-*m*-aminophenol (classes 2 and 3).

These classes of compounds are used to procure smooth deposits free from treeing. In addition, compounds are sometimes added for other purposes such as stabilizing and solubilizing the addition agents and as anti-oxidants for preventing oxidation and sludging of the tin, thereby keeping the solution clear. Some agents such as fluorides and tartrates, while keeping the solution clear and free of precipitated stannic compounds, do so by holding the stannic tin in solution and therefore are only effective for a certain length of time depending on the concentration of the agent. For actually preventing the oxidation of tin some of the well recognized anti-oxidants are effective. Catechol, resorcinol, naphthol, and some of the amines have been used for this purpose. Many of the addition agents used to suppress

tree formation are also anti-oxidants. Cresol sulfonic acid will act as an anti-oxidant and also as a solubilizer for some of the addition agents.

Since there are many types of addition agents, and since each must be added to the bath and subsequently operated under a specific set of conditions peculiar to that addition agent, it is difficult to make any statement concerning the rate of loss from the bath. However, several specific examples can be given. Hothersall and Bradshaw⁴⁸ report that an addition agent prepared by sulfonating o-cresol was removed fairly rapidly on working: "after the passage of 20 ampere-hours per liter, deposits from the best solutions had deteriorated markedly." Another addition agent composed of β -naphthol and gelatin had to be replenished after passage of 250 amp-hr/l.

It should be realized that under ordinary plating conditions the addition agent actually used up or occluded by the plate is negligible compared to that lost by drag-out (and hydrolysis in the case of glue or gelatin). Therefore the rate of loss from the plating bath will depend on the area and shape of the work plated. In one proprietary installation, it is necessary to add equal amounts of stannous sulfate and addition agents daily. Since the stannous sulfate is needed only to replenish that lost by drag-out, it is probable that the same is true of the addition agent.

FORMULAS

As in other plating baths, the concentration of the chief constituents of the acid tin bath may vary greatly, depending upon the current density required and other specific conditions. Likewise, when the concentration of one constituent of the bath is changed, the concentration of the other components may be changed proportionately. However, the ordinary limits are as follows: stannous sulfate, 30 to 90 g/l; sulfuric acid, 30 to 150 g/l; gelatin or glue, 0.5 to 10 g/l; cresol, 0.5 to 10 g/l; sulfonated cresol, 10 to 100 g/l; β -naphthol, 0.5 to 1 g/l; resorcinol,⁴⁸ 20 g/l; $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$,¹² 50 to 350 g/l; aloin,¹² 1 to 3 g/l. Of course, as previously explained, a bath will ordinarily contain not more than three of the above listed addition agents. A typical example may be mentioned: stannous sulfate, 54 g/l; sulfuric acid, 100 g/l; cresol sulfonic acid, 100 g/l; β -naphthol, 1 g/l; gelatin, 2 g/l. For use at higher current density, the concentrations may all be increased proportionately, although increases in concentration of sulfuric acid and addition agent are more effective in permitting higher current densities.

OPERATING CONDITIONS AND CHARACTERISTICS

The acid sulfate tin bath is usually operated at cathode current densities of 10 to 40 amp/sq ft, depending on the concentration, the nature of the addition agent, and type of deposit desired. With agitation, and where only thin deposits are desired, 1000 to 2000 amp/sq ft can be used. For ordinary work, cathode rod agitation is generally used, but even air agitation has been used without excessive oxidation of the tin in the sulfate bath.

The bath is ordinarily not heated except where the climate necessitates it. The best temperatures are between 20° and 30°C. There is a tendency for oxidation of stannous to stannic sulfate. This tendency is, of course, increased at the higher temperatures, and temperatures above about 40°C are definitely detrimental. Most addition agents and addition salts used in the acid bath have the property of retarding this oxidation.

Since the acidity of the acid tin bath is very high and since the concentration of sulfuric acid is not critical, the pH is not taken. For instance, a change in concentration of 10 ml/l of sulfuric acid in the acid tin bath is much less important than a change in concentration of 1 ml/l in a nickel bath.

EFFICIENCY, THROWING POWER, AND COVERING POWER

The efficiency of the acid tin bath is one of its chief advantages and has already been mentioned. The throwing power can vary widely, depending mostly on the addition agents used and on their concentration. The throwing and covering power of a bath containing no addition agent is very poor. When gelatin is added alone or when one of the aromatic addition agents is added alone, the throwing power and covering power increase; when both the colloid and the aromatic compound are added, there is a further increase in covering power. This is shown in Table 1, along with the throwing power of other common baths, including the alkaline stannate bath. The throwing power was determined in the Haring and Blum cell, with a linear ratio of 5, and results calculated by the British Standards Institute's formula and the Haring and Blum formula. The covering power was determined by the method of the Tin Research Institute,⁵² and is defined as the minimum current density for complete covering of a copper cathode in depositing 0.00005 in. of tin. Similar to other solutions, the initial throwing power can depend on the basis metal; this effect is shown in Table 2. Such short time measurements can-

not be accurate, but the results show a definite difference due to the basis metal.

The results in Tables 1 and 2 should be interpreted with the limitations of the methods of measurement in mind; no thoroughly satisfactory quantitative measure of "throwing power" is available.

TABLE 1. THE THROWING POWER OF THE ACID TIN BATH AS COMPARED WITH THAT OF OTHER BATHS

No	Bath Composition	Conc., g/l	Temp., °C	Current Density, amp/sq ft	Throwing Power		Covering Power, amp/sq ft
					H. & B.	B.S.I.	
1	SnSO_4 H_2SO_4	50 50	25	20	-34	-17.5	40
2	Same as 1 plus gelatin	2	25	20	47	41.5	15-20
3	Same as 1 plus cresol	3	25	20	40	33.3	14.3
4	Same as 1 plus cresol	6	25	20	33.3	26.3	25-30
5	Same as 1 plus cresol plus gelatin	6 2	25	20	47	41.5	1-2
6	Proprietary soln. ²⁸		25	20	40	33.3	38.0
7	$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ NaOH Na acetate	90 10 15	60	20	44	41.5	
8	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ H_3BO_3 pH 5.7	250 37.5 37.5	54	20	68	74	
9	Same as 8 pH 3.0		54	20	4	2.5	
10	Same as 8 pH 3.0		54	20	-6.2	-3.7	
11	Proprietary bright nickel pH 3.0		54	20	0	0	
12	CuCN Free CN Na_2CO_3 pH 12.5	22.5 5.7 22.5	54	20	61	62	
12	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ H_2SO_4	200 52.5	25	20	10	6.7	

CONDUCTIVITY

The acid tin bath ranks among the highest conducting of metal plating solutions. Depending on the anode area, the voltage required at 10 amp/sq ft is approximately 0.6 v, and at 40 amp/sq ft it is 1.6 v. An increase or decrease in the anode-to-cathode spacing has very little effect on the voltage because of the high conductivity of the solution. The specific resistance for both the sulfate and the fluo-

TABLE 2. INITIAL THROWING POWER ON VARIOUS BASIS METALS AS DETERMINED IN THE HARING AND BLUM CELL

SnSO_4 6 oz/gal
 H_2SO_4 6 oz/gal
 Addition agent ²⁸ 6 oz/gal
 Temperature 70°F

Basis Metal	Linear Ratio	Current Density, amp/sq ft	Time, sec	Throwing Power	
				H. & B.	B.S.I.
Buffed Cu	5	20	20	54	51
Matte Cu	5	20	20	48	43
Bright Cu Plate	5	20	20	48	43
Semi-matte Cu	5	20	20	48	43
Semi-matte Cu	2	20	20	25	33
Steel	5	20	20	28	21
Steel	2	20	20	20	25
Steel	5	10	40	16	11
Steel	5	30	13.3	38	31
Tin	5	20	20	40	33

borate bath for a tin content of 33 g/l and acid content of about 60 g/l will approximate 4.0 to 4.5 ohm-cm.

MAINTENANCE AND CONTROL

For best results the solution should be filtered frequently, especially if the most corrosion resistant and pore-free deposits are desired. It is common practice however to filter only two or three times a year, and for some applications this may be satisfactory. The suspended matter is largely stannic or basic stannic sulfate which is formed at the anode or by air oxidation. Suspended matter may also be formed from certain slightly soluble addition agents.

PURIFICATION

Since the acid tin bath can tolerate a large amount of contamination, a purification step is rarely necessary. The usual metallic impurities have practically no effect on the deposit, although a high copper contamination may accelerate oxidation of the stannous sulfate. Zinc has no visible effect. Chlorides dull the luster of the deposit and, if present in large amounts (say 15 to 20 g/l sodium chloride), may cause very crystalline deposits.

PHYSICAL CONTROL OF BATH

While in many cases the bath can be controlled very accurately by chemical analysis, it is frequently advisable to run plating tests on the solution. When plating tests are performed, attention is usually directed to three factors: (1) the general appearance of the deposit; (2) the maximum current density possible; and (3) the throwing power. The last may easily be determined qualitatively by use of a Hull cell or by plating a panel in a beaker of solution containing one anode and noting the time for complete coverage of the back of the panel. Throwing and covering power are usually dependent upon the addition agent concentration.

The Tin Research Institute⁵² states that the addition agent may be controlled simply by observing three factors:

The Voltage of the Bath. This decreases as the addition agent concentration decreases. Fresh quantities of addition agent should be introduced before the voltage has decreased by 0.2 v under the voltage of the freshly prepared solutions.

Surface Texture of the Tin Deposit. As the addition agent is consumed, the grain size of the deposit visibly increases.

Covering Power. Decrease in addition agent results in poorer covering power. Fresh additions should be made as soon as a test panel is not entirely covered after plating at 2 amp/sq ft for 12 min.

ANALYTICAL METHODS

All the constituents of the bath, including the addition agents, can be determined provided that the nature of the addition agents is known and a standard method is used.

Stannous Sulfate. (1) Pipette a 10-ml sample into a 500-ml flask; (2) dilute to about 200 ml; (3) add 25 ml of 1:1 hydrochloric acid; (4) titrate with standard 0.1 N iodine solution, using starch indicator:

$$\text{ml} \times N \times 10.74 = \text{g/l SnSO}_4$$

Stannic Sulfate. (1) Pipette 5 ml of sample into 500-ml sulfur flask with a side neck; (2) add 100 ml concentrated hydrochloric acid, 30 ml 50% sulfuric acid, 3 g of test lead and water to a volume of 300 ml; (3) stopper the flask and boil for 40 min to reduce the stannic sulfate; (4) while still boiling, submerge the outlet tube into 150 ml of saturated sodium bicarbonate solution and remove the flask from source of heat; (5) bicarbonate solution is sucked into the flask and thereby no air enters the flask while cooling; (6)

when room temperature is reached, titrate immediately with iodine; twice the reading minus that for stannous sulfate leaves the amount of iodine required by stannic sulfate:

$$\text{ml} \times N \times 15.54 = \text{g/l } \text{Sn}(\text{SO}_4)_2$$

ACIDITY

The determination for acidity is somewhat complicated, owing to the presence of sulfonic acids and amino acids, and a distinction should be made between total acid and free sulfuric acid. In a method reported by the Tin Research Institute⁵² the "total free acid" is determined by precipitating the tin salt with ethyl alcohol, diluting with water, and titrating with 1.0 N sodium hydroxide, using methyl orange indicator. This reading represents acidity caused by sulfuric acid and sulfonic acids; it is recommended that a definite ratio of these be added to the bath when the titration is low.

Free acidity may be determined directly by titrating with alkali in the presence of a large excess of neutral potassium oxalate with phenol red as an indicator. In this determination the change is gradual from yellow to pink or, if back titrating, from pink to yellow, so that a reference standard should be used. The cresol sulfonic acid can be corrected for after the cresol has been determined; then the free sulfuric acid may be calculated.

Cresol, or phenols in general, may be determined quite accurately by bromination under controlled and standardized conditions.

Protein or nitrogen may be determined by the usual Kjeldahl method; the result may be calculated to glue or gelatin provided the source of glue or gelatin is kept constant. After a protein addition agent has been in the solution for a long time it hydrolyzes to inactive amino acids. The active protein can be determined by analyzing for nitrogen before and after activated carbon treatment of aliquot samples. The more active protein is removed by carbon treatment.

EQUIPMENT

Lead-lined or, preferably, rubber-lined tanks are generally used, although for smaller work earthenware is satisfactory. (Lead equipment should not be used in fluoroborate solutions.) Frequently air agitation is used; this requires that a perforated pipe be installed in the bottom of the tank. In addition, some method of heating may be required in wintertime.

ANODES

Pure tin anodes are employed, and, unless the anode current density is above 25 amp/sq ft, no difficulty is encountered in anode corrosion. After some time of operation, the anodes become coated with a film of insoluble tin salts which, however, does not increase the bath voltage to any extent. This anode sludge may become detached, however, and may result in the solution becoming filled with suspended matter. If an excessive anode current density is used, a dark, slimy film sometimes develops on the anode, and this film increases the sulfate bath voltage tremendously. The anode area should be at least double the cathode area, and the anode current density less than 25 amp/sq ft. A small amount of halogen acid will prevent anode polarization. As previously mentioned, alkali metal sulfates may also be used for this purpose.

PREPARATION OF BASIS METALS

There is no special cleaning cycle required for tin plating, except possibly in the case of cast iron, and where special attention is focused on corrosion resistance. The ordinary alkaline cleaning followed by a rinse, acid dip, and rinse prior to plating is the usual cycle. With some cast irons it is necessary to give the parts a strike in cyanide copper or alkaline tin prior to the acid tin. A frequently used method incorporates the strike with the cleaner. This cleaner strike may be composed of 4 oz/gal of sodium stannate, 1 to 2 oz/gal of caustic soda, together with 3 to 4 oz/gal of metasilicate, orthosilicate, sodium carbonate, etc. Hedges⁵³ and Caulfield and co-workers⁵⁴ have described the effect of various pickling treatments on porosity. According to Hedges, the porosity by the thiocyanate test may vary 30 to 1 depending on the preliminary preparation of steel. With extreme care the sulfate bath produces less porous deposits, but the alkaline bath is less sensitive to pretreatment.

THE FLUOBORATE SOLUTION

In recent years fluoborate baths have come into prominence. The application of the tin fluoborate bath is as yet not thoroughly explored, and the published information^{33, 55, 57} is meager. Compared to the sulfate bath, the advantages of the fluoborate bath may be said to be in less sludging and a higher limiting current density. Actually,

When compared under similar conditions, the limiting current density of the fluoborate bath is not much different from that of the sulfate bath. The higher limiting current density of the fluoborate bath results from the higher tin and acid contents available. As in the sulfate bath, addition agents are necessary to avoid spongy deposits.⁵⁷

TABLE 3. COMPOSITION RANGES FOR THE TIN FLUOBORATE BATH

Tin (added as tin fluoborate concentrate)	5.4-11 oz/gal (40-80 g/l)
Free fluoboric acid	5.4-26.7 oz/gal (40-200 g/l)
Free boric acid	1.3-3.3 oz/gal (10-25 g/l)
Temperature	20-40°C (68-104°F)
Current density	20-400 amp/sq ft

Parkinson⁵⁶ has described the operation and performance of three baths containing the same tin and acid contents and using the following combination of addition agents:

- Gelatin, 6 g/l, plus β -naphthol, 1 g/l
- 4,4'-Dihydroxydiphenylmethane, 0.6 g/l
- 4,4'-Dihydroxydiphenylsulfone, 3 g/l

His preferred free acid content is 150 to 200 g/l, which gives a slightly lower limiting current density than 50 g/l of free acid but adds greatly to the stability of the bath. The acid content is not critical, and an approximate analysis is obtained by titrating 10 ml of the undiluted solution with standard sodium hydroxide until a faint permanent precipitate of tin hydroxide forms. The free boric acid content is not critical and is replenished amply by the free boric acid contained in commercial concentrates of tin fluoborate and fluoboric acid. Parkinson found that the anodes are relatively free of sludging if the bath is low in fluosilicate. A higher fluosilicate content will cause a voluminous anode sludge which is low in tin and high in silica.

Silica-containing materials of construction should not be in contact with the solution. Rubber-lined or bituminous painted tanks are usually used. Parkinson recommends a Polythene lining and anode bags of Terylene (I.C.I. Ltd., Plastics Div.).* Silica-type filter aids should not be used, but washed cellulose-types have proved satisfactory. Other materials of construction which have given indications of being suitable are Karbate, tantalum, and special high alloy stainless steels.

* "Dacron" and "Fiber V" are United States equivalents.

TESTS OF DEPOSITS *

In the tin plate industry it is common to refer to tin thickness in terms of weight per base box. A base box consists of 112 sheets with dimensions of 14 by 20 in. (33.6 by 50.8 cm). This is an area of 435 sq ft (40.4 sq m), and 1 lb per base box is equivalent to 0.00006 in. of tin in thickness. Table 4 gives base box data commonly used.

TABLE 4. BASE BOX DATA SHEET *

Base Box	Double Base Box
112 sheets—14 in. x 20 in.	224 sheets—14 in. x 20 in.
31,360 sq in. steel	62,720 sq in. steel
217.777 sq ft steel	435.5 sq ft steel
435.5 sq ft surface	871 sq ft surface

TIN

	0.5	1.0	1.5
Weight of coating, in lb/base box	0.5	1.0	1.5
Weight of coating, in oz, for 0.459 base box, or 100 sq ft of steel	3.66	7.32	11.0
Weight of coating, in oz, for 0.2295 base box, or 100 sq ft surface	1.83	3.66	5.5
Coating thickness, in.	0.00003	0.00006	0.00009
Plating time, min., at 30 amp/sq ft	0.5	1.0	1.5

TERNE—20% Sn, 80% Pb

$$1 \text{ oz/sq ft} \times 27.2 = \text{lb/double base box}$$

$$\text{oz/sq ft} \times 0.0000585 = \text{thickness, in inches (one side)}$$

LEAD

$$1 \text{ oz/sq ft} \times 27.2 = \text{lb/double base box}$$

$$\text{oz/sq ft} \times 0.0000528 = \text{thickness, in inches (one side)}$$

* Weight base box, 28-gage tin plate, about 138 lb.

The most important tests on tin plate are for porosity which is dependent for the most part on thickness of the deposit and condition

* *Editor's note.* Apparent discrepancies between this discussion and the corresponding one on pages 402 and 403 are due to the fact that here we are principally concerned with the thinly coated "tin plate" for tin cans, whereas the other discussion is concerned with general job plating. This difference in emphasis reflects the principal fields of usefulness of the respective baths.

f the basis metal. These are of about equal importance. Egeberg and Promisel⁵⁸ report that from alkaline solutions the porosity was negligible with a thickness of 0.00005 in., and from a carefully filtered acid solution this minimum thickness could be reduced to 0.00001 in.

Macnaughtan and co-workers⁵⁹ have determined the porosity of various tin coatings 0.00012 in. in thickness; they class them in the following order of increasing porosity: (1) composite coatings; (2) bright acid tin deposits; (3) smooth acid tin deposit; (4) hot-dipped coating; (5) alkaline tin deposit; (6) rough matte acid tin deposit. The composite coating obtained by plating tin on hot-dipped tin was decidedly the best. On stretching the tin-coated steel, the order is changed to: (1) composite tin coating; (2) hot-dipped coating; (3) smooth matte acid tin coating; (4) rough matte acid tin coating; (5) alkaline tin coating; (6) bright acid tin coating. With heavier deposits, the alkaline tin deposit gave slightly less porosity than the acid tin deposit. Results in the laboratory indicate that there is no difference in the porosity or protective value of the two deposits, provided that the acid tin deposit is thoroughly rinsed.

One point of difference between hot-dipped and electroplated tin coatings is the alloy zone between the tin and the basis metal. In the case of a steel basis metal, this alloy is said to consist of the compound FeSn₂, and it is possible that its presence affects the comparison between porosity and protective value of the coatings. Another cause of discrepancy at times in comparing the porosity of hot-dip tin and electroplated tin coatings is the fact that, compared to plated tin, certain hot-dipped tin is very difficult to clean thoroughly. This is probably due to a film of vegetable oil remaining on the surface and in the pores of the deposit after the hot-dipping process.

The determination of porosity of tin coatings has been thoroughly described by Egeberg and Promisel,⁵⁸ by Vaurio, Clark, and Lueck,⁶⁰ and by Hoare,⁶¹ so that only mention need be made of the several methods.

1. The hot water test, whereby the specimen is cleaned and immersed in an upright position in distilled water at a temperature of 95°C for 6 hr. Reddish brown spots are formed which are very adherent and may be easily counted.*

2. The ferricyanide test, whereby the specimen plate is immersed in a ferroxyl solution; or the plate is covered with prepared filter paper, placed in contact with it, and brushed with distilled water. The number and size of the blue spots are an indication of the degree of porosity.

* The pH of the water must always be the same to insure comparable results. A change in pH makes a very decided difference in the results.

3. The hydrogen evolution test, by which is measured the time to collect 5 ml of hydrogen when a test specimen is immersed in 1 N hydrochloric acid at 57°C.

4. Immersion of the specimens in boiling dilute solution of copper sulfate. The sites of the pores are revealed by rust and copper spots.

5. Gire's⁶² test, whereby the specimen is made the anode in a 0.5 to 0.1 N solution of sodium-hydrogen sulfide for 10 min.

6. The salt spray test, which may also be used for tin plate but, like the other tests, should not be considered indicative of the comparative service value at all times.

More recent publications on porosity of tin and its determination are given by Baier and Hoar⁶³ and Kerr and co-workers.⁶⁴ Kerr and associates⁶⁵ determined the effect of tin content, cresol sulfonic acid, current density, temperature, and wetting agents on porosity. Kerr and co-workers⁶⁶ determined the effect of thickness between 2 and 133 oz per base box on porosity by different methods. They showed that the porosity was roughly inversely proportional to t^3 (t = thickness) by the thiocyanate test, to t^2 by the hot water test, and to t by humidity, salt spray, and outdoor tests. For coatings of less than 12 oz per base box the deterioration was rapid in all tests.

The thickness of tin coatings can be determined microscopically if care is taken not to "spread" the tin while polishing. If the specimen is sufficiently uniform in shape so that the area can be determined, the average thickness can be determined by stripping the specimen in concentrated hydrochloric acid containing 20 g/l of antimony oxide. By weighing the specimen before and after stripping, the thickness can be calculated. The tin may also be stripped by treating anodically in a 5 to 10% solution of sodium hydroxide. For heavier deposits (over 0.0002 in.) and for certain shapes, one of the best methods is to pick out a diameter on the part which can be measured with a micrometer before and after plating or before and after stripping. Of course, this method cannot be used on a flat specimen, owing to the probable change in contour, but for round articles such as pistons the method can be made simple and accurate.

Hanna⁶⁷ gives an excellent summary of fifteen methods, with references, which have been proposed for determining the thickness of tin deposits including electrolytic, solvent, magnetic, and drop methods. An instrument involving deplating of the specimen, with automatic endpoint indication, is available.*

* Kocour Co., Chicago, Ill.

IMMERSION TINNING

FREDERICK A. LOWENHEIM *

For applications which require only a very thin film of tin, principally for decorative purposes, immersion processes are extensively used. Such articles as pins, paper clips, buttons, and small electrical parts are representative of such uses. Two important industrial uses of immersion tin coatings are the so-called "liquor finish" on steel wire and the tinning of aluminum alloy pistons for internal combustion engines. In addition, immersion coatings find several specialty applications, such as tinning the inside of copper tubing, which would not be susceptible to ordinary electroplating methods.^{1,†}

IMMERSION AND CONTACT PROCESSES

Immersion tinning is a very old art, and the number of "recipes" which appear in the literature is correspondingly large. In addition to journal articles, all the standard texts include such formulas.²⁻¹¹ For their operation many formulas rely on direct contact between the work and pieces of tin or zinc in the solution, and are thus in effect electrolytic methods, with the outside source of current replaced by a self-contained local couple. Where the contact metal is tin, the solution itself often contains no tin compound, reliance being placed on the solution and subsequent deposition of the tin metal; where the contact metal is zinc, the solution must contain a tin salt.

SUGGESTED FORMULAS ‡

1. Stannous chloride, § $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 3.5 oz/gal (25 g/l)
Cream of tartar, $\text{KHC}_4\text{H}_4\text{O}_6$ 1.3 oz/gal (10 g/l)
Small pieces of zinc in contact with the work, in a barrel at about 80°C; time, 2-4 hr.

* Metal & Thermit Corporation, Rahway, N. J.

† References for this portion of the chapter will be found on pages 433 and 434.

‡ See also Refs. 2, 4-12.

§ Anhydrous stannous chloride, SnCl_2 , may also be used. For each 10 parts of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ substitute 8.3 parts of SnCl_2 .

2. Cream of tartar, $\text{KHC}_4\text{H}_4\text{O}_6$ 0.2 oz/gal (1.5 g/l)
 Sodium chloride, NaCl 0.4 oz/gal (3 g/l)

Work and perforated sheets of tin are piled alternately in the solution, kept at 90°C or higher for 3 to 5 hr. The solution itself contains no tin and is discarded after each batch.

3. Stannous chloride,* $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 4 oz/gal (30 g/l)
 Sodium hydroxide, NaOH 8 oz/gal (60 g/l)

The stannous chloride and sodium hydroxide are dissolved separately; the sodium hydroxide solution is then added, with stirring, to the tin salt solution; the precipitate first formed redissolves to give a solution of essentially sodium stannite, NaHSnO_2 or $\text{Na}_2\text{Sn}(\text{OH})_4$. This formula may be used similarly to formula 2; but, since stannite solutions are essentially unstable, brass will be tinned in this solution by simple immersion, without the tin metal contact.

The three formulas above refer primarily to the tinning of brass articles. When iron or steel is the basis metal the following is applicable.

1. Stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ * 2 oz/gal (15 g/l)
 Sodium sulfate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ 21 oz/gal (160 g/l)
 Hydrochloric acid, HCl 0.13 fl oz/gal (about 1 ml/l)

This solution is heated to boiling; the heating is then discontinued and the work, alternating with layers of perforated zinc sheets, is placed in it for about 45 min. The solution is discarded after each batch.

It will be noted that all the above formulas call for rather extended periods of immersion and high temperatures. Some recently developed solutions have the advantage of being operable at room temperature and requiring only a few minutes' immersion.

5. Stannous chloride,* $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 0.7 oz/gal (5 g/l)
 Sodium hydroxide, NaOH 0.75 oz/gal (5.6 g/l)
 Sodium cyanide, NaCN 7 oz/gal (50 g/l)
 Room temperature; time 1-2 min

This bath has been patented¹³ and is discussed in the technical literature^{1, 14, 15} for the tinning of copper or copper alloys. As in almost all immersion processes, the thickness of coating is limited; but in this case the inventors have given data on the thicknesses obtained at different times of treatment.¹⁶ (See Table 1.)

* Anhydrous stannous chloride, SnCl_2 , may also be used. For each 10 parts of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ substitute 8.3 parts of SnCl_2 .

6. Stannous chloride,* $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 1.3–2.7 oz/gal (10–20 g/l)
 Thiocarbamide (thiourea), $\text{CS}(\text{NH}_2)_2$ 11–12 oz/gal (80–90 g/l)
 Hydrochloric acid, HCl 1.3–2.7 oz/gal (10–20 ml/l)
 Temperature, 50°C (122°F) to boiling; time, 5 min

In this patented formula,¹⁶ the thiourea apparently performs the same function as the cyanide in formula 5; that is, it increases the tendency of the copper basis metal to dissolve by complexing the copper ions.

7. A very similar bath, also patented,¹⁷ contains:

- Stannous chloride,* $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 0.7 oz/gal (5 g/l)
 Thiourea, $\text{CS}(\text{NH}_2)_2$ 6.7 oz/gal (50 g/l)
 Sulfuric acid, H_2SO_4 2.7 oz/gal (20 g/l)
 Room temperature; time, 5–30 min

Data on deposit thicknesses obtainable by formulas 6 and 7, as given in the patent disclosures, are included in Table 1.

TABLE I. THICKNESS OF TIN COATING FROM IMMERSION FORMULAS 5, 6, AND 7

Time of Immersion	Coating Thickness, thousandths of an inch		
	No. 5	No. 6	No. 7
1 min	...	0.024	...
2 min	...	0.037	...
3 min	...	0.047	...
4 min	...	0.053	..
5 min	0.004	0.060	0.008
15 min	0.006	...	0.015
30 min	0.009	...	0.018
1 hr	0.014
2 hr	0.021
24 hr	0.140	...	0.125

8. Another solution for the immersion tinning of copper and brass recently introduced is¹⁸

- Potassium stannate, $\text{K}_2\text{Sn}(\text{OH})_6$ 8 oz/gal (60 g/l)
 Potassium cyanide, KCN 16 oz/gal (120 g/l)
 Potassium hydroxide, KOH 1 oz/gal (7.5 g/l)
 Temp. room to 65°C; time 2–20 min

It should be noted that these methods are applicable only to copper and copper-base alloys; and it is obvious that the coating thicknesses

* Anhydrous stannous chloride, SnCl_2 , may also be used. For each 10 parts of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ substitute 8.3 parts of SnCl_2 .

obtainable are in no respect comparable with those produced by electroplating. If a bright deposit is required, the basis metal should be bright to start with, since the deposits are so thin that in most cases the character of the underlying surface is not altered appreciably.

A recently revived method of "contact tinning" applicable to many different basis metals is to hang the work in the conventional stannate bath in contact with aluminum, such as by suspending it on aluminum wires.¹⁹

TINNING OF ALUMINUM ALLOYS

Aluminum and its alloys can be tin plated by any of the methods suitable for plating on aluminum; but, in the particular case of aluminum alloy pistons for internal combustion engines, the tin coating is applied by an immersion process which does not involve the usual pre-treatments necessary for electroplating methods. The purpose of the tin coating is to act as a lubricant during the running-in period; a major proportion of all aluminum alloy pistons is tinned by the following process or variations of it.

The parts are first cleaned in one of the cleaners specially formulated for aluminum; after a cold water rinse they are dipped in 20% nitric acid for about 20 sec; after another cold water rinse they are tinned by immersion in a sodium or potassium stannate solution, originally about 6 to 9 oz/gal for 3 to 4 min, at a temperature of 50° to 75°C. A cold and a hot rinse complete the process. Coatings are matte white, of thicknesses considerably greater than those obtained by usual immersion techniques: up to 0.0002 in. or more.

There are various means of controlling this process to compensate for the gradual decrease in tin content and corresponding increase in equivalent free alkali as the work is put through the bath. Free alkali should be maintained below 1.3 oz/gal, and this may be accomplished by adding acetic acid as needed.²⁰ The decrease in tin content may be made up by periodic additions of stannate, by raising the temperature, or both. In any case, baths are generally discarded periodically, since impurities and sludge build up to such an extent that making up a new solution is more economical than attempting to rectify an old one. There are indications that potassium stannate, because of its greater stability, gives solutions which run longer before discarding becomes necessary, thus more than compensating for the higher cost compared with sodium stannate. The process has been described in the literature²¹⁻²³ in somewhat more detail than can be given here.

Recently the use of stannous sulfate-hydrofluoric acid solutions has been advocated as an improvement over the foregoing process.²⁴ Stan-

stannous chloride-ammonium alum²⁵ and stannous fluoborate or fluosilicate²⁶ have also been recommended.

LIQUOR FINISHING OF STEEL WIRE

The so-called "liquor finish" is applied to steel wire for two purposes: as a drawing lubricant and as a decorative finish for such articles as hairpins and clips. The deposit is normally a copper-tin alloy, produced from a solution such as

Stannous sulfate, SnSO_4	1 oz/gal (7.5 g/l)
Copper sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	1 oz/gal (7.5 g/l)
Sulfuric acid, H_2SO_4	10-30 g/l or 1% 3% by weight

Variations in color are produced by varying the copper sulfate content; the higher the copper, the redder the deposit. The process requires a few minutes at room temperature.

When a white finish is desired, the following solution may be used:

Stannous sulfate, SnSO_4	0.1-0.3 oz/gal (0.8-2.5 g/l)
Free sulfuric acid, H_2SO_4	0.7-2 oz/gal (5-15 g/l)
Temperature, 90°-100°C— time, 5-20 min	

For a full description of the process see Ref. 27.

TIN ALLOYS

FREDERICK A. LOWENHEIM *

The general principles of alloy deposition are discussed elsewhere in this volume, and a word may be said as to why a special section is devoted to the alloys of tin. Reference to Chapter 3 will show that a considerable portion of the work that has been carried out in this field has been of academic or theoretical rather than practical interest, and that relatively few processes have been developed to the commercial stage. The principal exceptions to this statement are the deposition of brass, of some gold alloys, and of some alloys of tin, notably with copper, with lead, with nickel and with zinc. Tin-lead alloy plating is considered on pages 291 to 296; the processes for plating the other three tin alloys mentioned merit somewhat more detailed treatment here.

The alkaline stannate bath lends itself admirably to adaptation for the plating of alloys with those metals which can be deposited from cyanide solutions: the tin-copper and tin-zinc processes are of

* Metal & Thermit Corporation, Rahway, N. J.

this type. Although tin-nickel alloys can be deposited from stannate-cyanide solutions¹ such baths are not practically operable and the tin-nickel process is of an entirely different nature.

In addition to the three discussed below, there are several tin alloy plating processes—mostly involving tin, copper, and zinc—which because of their patented or proprietary nature are not considered here. It should also be stated that the discussions herein are necessarily brief and incomplete; anyone seriously contemplating the installation of one of these baths may obtain the literature and technical advice offered by the Tin Research Institute or the Metal & Thermit Corporation.* This literature also contains instructions, omitted here, for analytical control of the baths.

TIN-COPPER OR SPECULUM

Alloys of tin and copper in the 90% Cu-10% Sn range are, of course, the commercial bronzes and are used on a very large scale. They can be electrodeposited² and have been used to a limited extent as stop-offs in the nitriding of steel.³ The speculum alloy, however, contains 40 to 60% Sn; the optimum composition is 45% Sn, 55% Cu. This alloy is white, closely resembling highly polished silver; it is recommended for decorative applications for indoor use, such as bathroom fixtures, ashtrays, and tableware. For such applications its tarnish resistance and protective qualities are claimed to be excellent; it is not recommended for outdoor exposure, particularly in industrial atmospheres. As plated, speculum is matte to semi-bright but is easily buffed to a high luster.†

Speculum is plated from a bath of the following composition.⁴

	Ounces per Gallon	Grams per Liter
Sodium stannate, $\text{Na}_2\text{Sn}(\text{OH})_6$ (Tin metal)	12.7 5.3	95 40
Copper(I)cyanide, CuCN (Copper metal)	1.43 1.0	11 7.5
Free sodium cyanide, NaCN	2.3	16
Free sodium hydroxide, NaOH	2.0	15

Control Limits

Tin	5.1-5.6	38-42
Copper	1.1-1.4	7.5-8.5

* Tin Research Institute, 492 West 6th Ave., Columbus 1, Ohio. Metal & Thermit Corp., 100 East 42 St., New York 7, N. Y.

† It has been reported that a "bright speculum" has been developed, but no details of the process have been published.

	Ounces per Gallon	Grams per Liter
Free NaCN	2.14-2.4	16-18
Free NaOH	1.9-2.14	14-16
Temperature, 65°C ± 2°		
Cathode current density, 15-25 amp/sq ft		
Anode current density, see text		
Efficiency, about 60%; time to plate 0.001 in., about 20 min		
Recommended thickness: 0.0005 in. on brass, copper, etc.		
0.001 in. on steel		

Since anodes of the same composition as the deposit do not dissolve well, two separate anode circuits with individual control have to be used. The tin anodes must be maintained in the polarized or "filmed" condition as for stannate tin plating, and thus the voltage in the tin anode circuit is higher than that in the copper anode circuit. Three-quarters of the total current is passed through the tin circuit, one-quarter through the copper circuit; current density on the copper anodes is maintained at about 5 to 10 amp/sq ft, and on the tin anodes at 15 to 20 amp/sq ft.^{5,6}

It has been proposed to regulate the anode reaction by means of a time cycle instead of the dual circuit;⁷ the current is passed alternately through the copper and the tin anodes. Another proposed means for avoiding the dual circuit is to employ insoluble anodes, or anodes of either copper or tin, and to regenerate the bath chemically by the addition of copper stannate.⁸ For a complete discussion of the process and for detailed working instructions, see Refs. 5, 9 to 12.

TIN-NICKEL

The recently developed tin-nickel alloy electroplate is reported to possess several outstanding qualities which should render it quite attractive to platers if practical experience substantiates the claims made for it. These include: (a) it is bright or nearly so as deposited if the basis metal is bright; (b) it is exceptionally tarnish-resistant; (c) it is practically inert to a wide variety of reagents; (d) the bath has good throwing power and a relatively high rate of deposition; (e) the deposit is of pleasing appearance, of a much warmer hue than chromium.

The outstanding properties of this deposit are evidenced only when plates are substantially pore-free: porous deposits are liable to early failure. Production of pore-free deposits can be ensured by frequent or, better, constant filtration of the bath through a bed of activated carbon and by bagging the anodes.

The alloy as deposited is the intermetallic compound NiSn, containing 65% Sn, 35% Ni. The deposit composition is remarkably constant over fairly wide ranges of bath composition and operating conditions.

The alloy is plated from the following solution.^{13 15}

	Ounces per Gallon	Grams per Liter
Stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ or	6.7	50
Stannous chloride anhyd., SnCl_2 (Tin metal)	5.7 3.5	42 26
Nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Nickel metal)	40 10	300 75
Sodium fluoride, NaF (Fluorine)	3.75 2	28 15
Ammonium bifluoride, NH_4HF_2 (Fluorine)	4.67 3.2	35 24
Total fluorine in bath	5.2	39
pH (colorimetric), 2.5		
Temperature, 65°C (150°F)		
Cathode current density, 25 amp/sq ft		

Separate anodes of tin and nickel are used, with about equal amounts of current being passed through each. Although the early work resulted in the recommendation that the tin and nickel anodes be hung from separate bus bars with individual control, it has been shown more recently that they may be hung from the same bar and control exercised by varying the area ratio of tin to nickel. The tin anodes should be removed during extended idle periods. The deposited alloy, NiSn, does not appear as a separate phase on the thermal equilibrium diagram of the tin-nickel system; this compound has so far been produced only by electrodeposition.¹⁶ When it is attempted to cast anodes of the composition NiSn, a two-phase system is produced consisting probably of $\text{Ni}_3\text{Sn}_4 + \text{Ni}_3\text{Sn}_2$; unfortunately these two phases do not corrode in the solution with equal ease, hence the necessity for separate tin and nickel anodes. Anode current density may be up to 50 amp/sq ft.

In the preparation of the solution several purification steps are recommended, for details of which the working directions should be consulted.¹⁷ High purity solutions are necessary for proper operation of the process.

Because of the corrosive nature of this solution and the toxic character of its fumes—it contains free hydrofluoric acid and elevated temperatures are used in its operation—careful consideration must

be given both to materials of construction and to protection of workmen. Materials which have been found satisfactory are rubber-lined steel and "Perspex."* Not all rubbers are suitable for linings, and a small scale test is recommended before proceeding with plant installations.¹³ Anodes may be bagged with "Terylene,"† but other materials such as nylon have been shown to be suitable. Heating may be by external water jacket or heat exchanger; if immersion heaters are to be used they should be heavily nickel-plated, as nickel is the only metal known to be sufficiently resistant to the solution.

"In the interests of health it is absolutely essential that the tank be provided with a thoroughly efficient exhaust system. Vaporisation can be substantially reduced by covering the surface of the electrolyte with small polythene tubes such as are used to cut down spray in chromium plating practice."¹³

The tin-nickel alloy can be plated directly over steel, but better results have been obtained with an intermediate coating of copper. The principal necessity in the operation of the process is the maintenance of a pure electrolyte, free of suspended matter and of organic contamination.

The behavior of tin-nickel coatings on exposure to the weather and to various reagents has been reported.^{15, 18} Analytical methods as well as working instructions are given in references 13 and 17. Hull cell tests are valuable in controlling the process.¹⁹

TIN-ZINC

The deposition of alloys of tin and zinc is not new, but credit must be given to the Tin Research Institute for the development of a successful commercial process. The electrolyte is a stannate-cyanide solution, which is easily prepared and controlled and not too critical in operation. Anodes of the same composition as the deposit are used, so that, except for somewhat greater need for analytical control, the process is hardly more complicated than stannate tin plating.

The alloy usually recommended, and upon which most intensive work has been done, is in the range 75 to 80% tin, remainder zinc. This deposit possesses these desirable properties which render its commercial possibilities attractive: it offers excellent corrosion protection, comparable with zinc or cadmium; it does not so readily form the voluminous white corrosion product typical of zinc.²⁰⁻²⁴

* "Lucite" is the equivalent in the United States.

† "Dacron" and "Fiber V" are similar in the United States.

It is cheaper than cadmium; basically, both tin and zinc are more "available" than cadmium, though governmental restrictive measures have in recent years tended to confuse the issue. The solderability of the coating is excellent, being better than that of cadmium and at least equal to that of tin; and it surpasses tin in retention of good solderability on storage. The relative value with respect to corrosion of zinc, tin-zinc, and cadmium depends to some extent on the type of exposure.²⁴ The deposit is not bright; and, being an alloy, it demands somewhat more analytical control than the deposition of a single metal. Throwing power and covering power, and the basic operating factors of the process, are excellent.

The tin-zinc alloy deposit has also been reported to have excellent anti-friction characteristics which suggest its use as a bearing surface.²⁵

The solution first proposed for the plating of tin-zinc alloys was a sodium stannate-zinc cyanide bath of the following composition:²⁵⁻²⁷

	Ounces per Gallon	Grams per Liter
Sodium stannate, $\text{Na}_2\text{Sn}(\text{OH})_6$	9.5	72
(Tin metal)	4.0	30
Sodium hydroxide, NaOH	0.5 to 0.8	4 to 6
Zinc cyanide, $\text{Zn}(\text{CN})_2$	0.6	4.5
(Zinc metal)	0.33	2.5
Free sodium cyanide, NaCN	2.8	21
(Total NaCN)	3.7	28

Some difficulty was experienced when an attempt was made to repeat the English work in America, a difficulty which was finally traced to a difference in the quality of English and American sodium stannate.²⁸ This difficulty is completely avoided, and a bath of somewhat better characteristics with regard to speed and latitude in operation is obtained, by using potassium salts in place of sodium. The following bath is being used in still plating.²⁹

	Ounces per Gallon	Grams per Liter
Potassium stannate, $\text{K}_2\text{Sn}(\text{OH})_6$	16.0	120
(Tin metal)	6.0	45
Zinc cyanide, $\text{Zn}(\text{CN})_2$	1.4	10.5
(Zinc metal)	0.8	6
Potassium hydroxide, KOH	0.87	6.5
Free potassium cyanide, KCN	2.8	21
(Total KCN)	5.5	41

For barrel plating the bath is modified somewhat, as follows.

	Ounces per Gallon	Grams per Liter
Potassium stannate, $K_2Sn(OH)_6$	12.7	95
(Tin metal)	4.7	35
Zinc cyanide, $Zn(CN)_2$	1.8	13.5
(Zinc metal)	1.0	7.5
Potassium hydroxide, KOH	1.3	10
Free potassium cyanide, KCN	2.0	15
(Total KCN)	6.0	45

Working temperature of the bath is $65^{\circ}\text{C} \pm 2^{\circ}$ at cathode current densities for the sodium bath of 10 to 30 amp/sq ft, and for the potassium bath of 15 to 60 amp/sq ft. Anodes of the same composition as the deposit (80% Sn, 20% Zn) are used, at anode current densities of about 25 amp/sq ft. Anodes must be filmed, as in stannate tin plating; if not filmed, the deleterious results at the cathode are similar.

Throwing power of the bath is excellent, both with regard to metal distribution and "composition distribution"—the latter connoting the fact that the alloy composition is fairly constant on high and low current density areas.²⁷ Fortunately the composition of the deposit is not particularly critical; although 75 to 80% Sn is the aim, deposits in the range 70 to 85% Sn have very similar characteristics. When the deposit is too high in tin—in particular when the zinc content goes below 10%—some corrosion-protective properties are sacrificed, and, if too high in zinc, the solderability may suffer and the corrosion characteristics may approach those of zinc.

Mild steel equipment is satisfactory, and no special cleaning techniques are required. Rinsing after plating should be thorough, since the bath has a solvent action upon the deposit. The deposit may be "passivated" by immersion for a few seconds to a minute in 2% chromic acid solution at 50° to 80°C . This treatment improves the performance of the plate as measured by the salt fog test, but it may somewhat interfere with solderability and should be used with caution if this is an important factor in the application.

Since the bath operates at a somewhat high temperature for a cyanide solution, the cyanide should be checked rather frequently, as should the free alkali. Metal content may be checked at more infrequent intervals. General effects of the variables involved are:

Increasing temperature increases the tin content of the deposit, and increases the rate of cyanide breakdown. Decreasing tempera-

ture decreases the tin content, but also lowers the cathode efficiency; rather close temperature control is advisable, therefore, in view of these effects. Increasing free alkali increases the zinc content. Increasing free cyanide increases the tin content, up to a point beyond which further increase has little effect;²⁷ the bath as formulated contains a quantity of cyanide which is above this critical limit, so that minor variations in cyanide have little effect; if, however, the cyanide content is allowed to fall too far, small changes will have large effects upon the deposit and the bath will become difficult to control. The metal content of the bath exerts the expected effect upon the deposit composition; that is, increasing zinc metal increases the zinc content of the plate, etc.

More complete working instructions for the process as well as methods of analysis will be found in references 27 and 29.

Zinc

Per dollar of coating cost, zinc coatings confer more protection against atmospheric corrosion of iron and steel than any other coating. The efficacy of zinc depends on (1) its high resistance to atmospheric corrosion; (2) its galvanic protection of areas exposed by flaws or injuries to the coating,* and (3) the inhibition of corrosion by the presence of corrosion products of the zinc.†

Zinc coatings, with few exceptions, are applied only for the protection of iron and steel. Since zinc weathers to a drab gray color, its coatings are generally unsatisfactory where a permanently brilliant finish is desired. Recently, bright zinc finishes, preserved by clear lacquer or by treatment in chromate baths, have had decorative applications where the atmosphere is not unduly corrosive.

Only cadmium approaches zinc in its protection of steel surfaces. Although cadmium is sometimes less effective,‡ it may be preferred for its non-crusting corrosion products in marine service or for other special properties.

Zinc coatings have long been applied by dipping the article in molten zinc. The primary advantage of electroplating is the ability to apply zinc coatings of any desired weight according to the amount of protection desired. In hot dipping, the coating thickness is uncertain and is limited to a narrow range. Electrogalvanizing is frequently much less costly. Moreover, on simple shapes the coatings are much more uniform in thickness; since electroplated zinc is generally only slightly superior § to hot-dip zinc per unit of *actual* thickness, uniformity and thickness are the significant factors. Furthermore the heavy losses of zinc as dross in the hot process, which sometimes account for one-third of the zinc consumed, are completely avoided by electroplating. Plating baths are of two types: acid baths and alkaline cyanide solutions.

* H. H. Uhlig, *Chem. Eng. News*, **24**, 3154 (1946).

† R. S. Thornhill, *Ind. Eng. Chem.*, **37**, 706 (1945).

‡ E. E. Holls, *Metallurgia*, **35**, 30 (1946).

§ On the average, about 8 to 10%, according to tests conducted by E. H. Lyons, Jr. [*Trans. Electrochem. Soc.*, **80**, 387 (1941)], and data and discussion presented by C. D. Hocker and co-workers, *Proc. Am. Soc. Testing Materials*, **45**, 70 (1945).

Electroplated zinc coatings are substantially pure, ductile, and free from the brittle alloys characteristic of some hot-dip coatings. This feature permits the coated articles to be drawn, stamped, or otherwise formed, and precludes early failure of protection at damaged regions of the coating. The absence of incidental heat treatment avoids warping or change of temper of the steel. Electroplated screw threads need not be rechased, but the electroplate fails to "solder" or bridge over seams and joints. Sherardizing and zinc spraying are used for special purposes.

ACID ZINC

ERNEST H. LYONS, JR.,* AND HAMNETT P. MUNGER†

The most extensive use of acid zinc baths is in electrogalvanizing steel wire and strip. The advantages of the acid bath are its high plating rate^{1,‡} and low operating costs. However, compared with cyanide baths, acid baths have poor throwing power. When electroplating wire and flat-rolled steel products, throwing power is not a factor in securing uniform coatings. For this reason acid zinc baths have been very successful in coating these products. Acid zinc deposits are generally coarse-grained, but this does not affect the corrosion resistance. Since box strapping, stapling wire, and many other steel articles need only limited protection, thin, inexpensive coatings of zinc, 0.0025 to 0.013 mm (0.0001 to 0.0005 in.) thick, are adequate.² If such coatings are to be painted, even thinner coatings, as low as 0.0013 mm (0.00005 in.) thick, may be applied. For painted products special chemical treatments to form a paint-holding film (such as a phosphate coating) are necessary, since without them paint adherence is not satisfactory. The zinc prevents rusting at flaws and scratches in the paint, and is itself protected from early corrosion. Certain steel Venetian blinds are an example of such painted, zinc-plated surfaces.

For other purposes, heavier coatings, 0.0127 to 0.038 mm (0.0005 to 0.0015 in.) thick, are deposited.³ Electrogalvanized steel strip is formed into special channels and shapes such as flexible steel conduit (BX) cable. Electrogalvanizing of wire produces coatings with

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† Battelle Memorial Institute, Columbus, Ohio.

‡ References for this portion of the chapter will be found on pages 458 and 459.

greater uniformity, adherence, and ductility, and with a wider range of coating weight, than the old hot-dip methods permit; coatings heavier than 2.4 oz/sq ft are commercially applied.⁴⁻⁶ A considerable amount of electrogalvanized wire is drawn down to smaller gages after electrogalvanizing. The ampere capacity in the United States for wire and strip steel (including some strip lines converted from tin plating) exceeds 800,000 amp.

Large quantities of wire cloth (screening) are protected with 0.1 to 0.2 oz/sq ft of electrodeposited zinc which, in turn, is generally protected with a coat of varnish. Hardware, iron and steel castings, small manufactured parts, and a large number of other articles are extensively electrogalvanized in acid zinc baths. Electric conduit pipe, silo rods, tie rods and other structural parts, threaded pipe couplings, bolts, braces, hangers, hooks, and buckles are plated in acid zinc baths. Small bolts, nuts, rivets, washers, nails, etc., are electrogalvanized in acid baths in barrels, receiving coatings of 0.05 to 0.5 oz/sq ft.

DEVELOPMENT OF ELECTROGALVANIZING

About 1910 the early difficulties with cleaning metal surfaces and controlling of plating baths were solved. Improved electrolytes resulted in deposits of better appearance, so that applications for acid zinc plating began to increase extensively. The crude control methods were chiefly aimed at determining pH. Since then, the current densities have risen from 5 to 10 amp/sq ft to about 200 to 400 amp/sq ft, and as high as 2000 to 3000 amp/sq ft in some cases. The electrogalvanizing of steel strip became important in 1915,⁷ and of round wire in 1933.^{4-6,8}

In the thinner coatings, electrogalvanizing is finding greatly enlarged application. With the increasing price of zinc, the cost advantage of electrogalvanizing is even more pronounced. Since it also produces uniform coatings of higher quality, electrogalvanizing may be expected to displace the hot-dip method even more extensively. Comparatively little attention has been paid as yet to the possibilities of heavy coatings. Technological improvements which would permit the competition of electrogalvanizing in the heavy coatings field would be (1) ability to use a lower cost raw material as a source of zinc, (2) high current density electrolytes, and (3) better handling facilities for increased speed of electroplating. With its limited throwing power, acid zinc plating will hardly replace the hot dipping of such articles as pails, pipes, and fittings.

Although baths based on zinc fluoborate, perchlorate, or sulfamate have received some attention, almost all acid zinc plating employs

the sulfate bath, chloride bath, or a mixed chloride-sulfate bath. To furnish metal ions, zinc sulfate or zinc chloride is either purchased or prepared by dissolving zinc in acid. Concentrations of 32 to 54 oz/gal of $ZnSO_4 \cdot 7H_2O$ or of 10 to 32 oz/gal of zinc chloride are used. Although zinc sulfate is a moderately good conductor, chlorides of sodium, ammonium, zinc, or aluminum improve the conductivity somewhat.^{9,10} The addition of free acid improves the conductivity. Acetates and aluminum salts have sometimes been used as buffers.¹⁰

The most common addition agents are dextrin, licorice, glucose, and gelatin. Others which have been used are molasses; β -naphthol; goulac; cresylic acid; sulfonated cresols, phenols, and anthraquinone; sodium bisulfite; soaproot; silicic acid; caffeine; glycerin; and a variety of organic condensation products. Many others have been suggested. These substances are claimed to promote smoother, brighter deposits; to widen the operating ranges of temperature, pH, and current density; to restrain spray; and to control anode efficiency.

SULFATE-TYPE ACID BATHS

Typical compositions of the sulfate-type acid zinc plating bath follow:

Bath A ^a	Ounces	Grams	Bath C ^a	Ounces	Grams
	per Gallon	per Liter		per Gallon	per Liter
$ZnSO_4 \cdot 7H_2O$	32	240	$ZnSO_4 \cdot 7H_2O$	48	360
NH_4Cl	2	15	NH_4Cl	4	30
$Al_2(SO_4)_3 \cdot 18H_2O$	4	30	$NaC_2H_3O_2 \cdot 3H_2O$	2	15
Licorice	0.13	1	Glucose	16	120
Bath B ^a			Bath D ^a		
$ZnSO_4 \cdot 7H_2O$	54	410	$ZnSO_4 \cdot 7H_2O$	32	240
$AlCl_3 \cdot 6H_2O$	3	20	$NaC_2H_3O_2 \cdot 3H_2O$	2	15
Na_2SO_4	10	75	$Al_2(SO_4)_3 \cdot 18H_2O$	4	30
			Licorice	0.13	1

Considerable variations from the formulas may be made without appreciably affecting results. Barrel plating baths containing 4.5 lb/gal $ZnSO_4 \cdot 7H_2O$ have been used. The composition of two sulfate-type baths used in large scale plating of strip steel is given on page 453.

OPERATING CONDITIONS

CATHODE CURRENT DENSITY

For still tank plating, 10 to 30 amp/sq ft may be used; with agitation, higher current densities are permissible, especially on certain classes

of work. Special baths used for plating wire operate as high as 2000 amp/sq ft.⁴⁻⁶ The anode current density is not critical.

TEMPERATURE

For most purposes, 24° to 30°C produce the most lustrous deposits and the best throwing power; but, where these are unimportant, much higher temperatures may be used.

pH RANGE

The common operating pH is 3.5 to 4.5. It is not critical, but for uniform results it should be held within 0.3 unit. For barrel plating the pH should be greater than 5.0.

CURRENT EFFICIENCIES

Both anode and cathode current efficiencies are substantially 100%, and plant practice closely approaches this value. Certain impurities may cut the cathode efficiency, which may also drop at very low current densities (less than 0.1 amp/sq ft) on certain surfaces.¹¹

THROWING POWER

As measured in the Haring-Blum cell,^{10,12} the throwing power varies from -3 to 4%. Increasing the sulfate content of the bath has little effect on throwing power.^{9,10,13,14} A preliminary "strike" deposit from a cyanide zinc or cadmium bath often results in deposition in recesses which otherwise could not be coated in an acid bath.

CONDUCTIVITY AND POLARIZATION

The specific resistivity of zinc sulfate solutions in the recommended strengths is 18 to 23 ohm-cm at 25°C^{9,10} and is not much reduced by the customary additions. Polarization at both anode and cathode is quite low, less than 0.1 v.^{9,10,13-16}

MAINTENANCE AND CONTROL

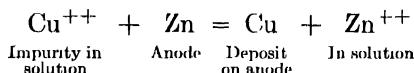
FILTRATION

Continuous filtration is customary in large, continuous plating installations, but not in still tank operations because in these operations suspended matter settles to the bottom during idle periods and thus rough deposits and unattractive blue color of the plate are avoided.

PURIFICATION

Although zinc deposition is quite sensitive to metallic impurities, this is seldom more than a transient problem in practice, because most

of the troublesome metals are plated out by displacement on the anodes during idle periods:



Deposited impurities on the anodes are eliminated by removing the anodes, dipping them in acid, and scrubbing. Precipitated impurities not removed in this way largely drop into the sludge but may redissolve anodically during operation, so that this automatic purification is less effective when the bath is in use. Arsenic, which is occasionally an impurity in the acid, is troublesome even though it may be volatilized as arsine as well as removed by displacement on the zinc.

In operation, iron salts are carried into the bath on the work, for rinsing is rarely complete after the acid treatment. The iron concentration in an operating bath is commonly 2 to 10 g/l; with higher concentrations, and especially at high current densities, iron is codeposited with the zinc, but it seems to have no noticeable effects on appearance, physical properties, or corrosion protection of the coatings.

When the pH exceeds 4, iron oxidized by dissolved oxygen often precipitates as hydrous ferric oxide, but this seems to have no effect on the electrodeposits. The precipitation may be used to remove excessive amounts of iron from the bath, pumping air through the bath or using hydrogen peroxide or manganese dioxide to accelerate the oxidation; traces of arsenic and other impurities are absorbed in the precipitate and will be removed. During electrolysis, dissolved ferric salts reduce the cathode efficiency, but they are quickly converted to the ferrous state at the zinc surfaces, and the efficiency is then restored.

At very high current densities traces of metallic impurities are much more troublesome. The purification process may be promoted by providing greatly enlarged zinc surface by stirring in zinc dust (which appears to be as effective as plating at low current densities, as is sometimes done with nickel baths). Tellurium, from tellurium lead piping, produces a poor color of the deposits.* Organic impurities, which also may be exceedingly troublesome, are removed, along with organic addition agents, by treatment with activated carbon. Rubber should always be tested in the bath before being used for tank linings. A new bath often shows better deposits after being used for several hours because of the elimination of impurities.

* Contrary to a previous report [*Trans. Electrochem. Soc.*, **89**, 290 (1946)], germanium is troublesome at high current densities; but it has never been detected in commercial baths.

PHYSICAL CONTROL

For *pH* determinations the glass electrode has practically replaced the quinhydrone electrode, but colorimetric methods are also common; the latter read 0.3 to 0.5 unit higher than the former, as in the case of nickel baths.

A zinc sulfate solution is always sufficiently acidic to attack the anodes slowly. As the acid is consumed, the *pH* rises until hydrous zinc oxide or basic salts precipitate and form a film on the anode so that further action is retarded. When the *pH* exceeds 4.2, the attack on the anodes becomes very slow, and it is rare to find a *pH* much above 5.

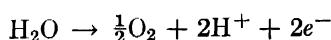
In operation, acid is added to lower the *pH*; and, as it is constantly but slowly consumed at the anode surfaces, it must be replenished periodically. Consumption runs about 15 to 75 ml of sulfuric acid (sp. gr. 1.84) for every 1000 l in 4 hr. Replenishments should be so made as to maintain a uniform *pH* throughout the bath. The *pH* is commonly between 3.5 and 4.5, although it may be much lower.

The steady consumption of acid corresponds to the continual formation of zinc sulfate, which tends to compensate for that lost by drag-out of the bath on the finished work. If the drag-out losses are excessive, so that the zinc content of the bath becomes too low, then more acid must be added during idle or even working periods, or zinc sulfate as such must be added. Continual need for such corrections indicates extraordinary losses of solution, as by leakage. If, on the other hand, the zinc content becomes too high, the rate of acid attack on the anodes must be decreased by operating at lower temperatures, or by using purer anodes, which are less actively attacked. Components of the bath other than zinc sulfate must be replenished as they are lost by drag-out; usually such corrections are not at all critical.

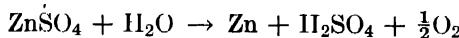
For barrel plating, acid zinc baths must be operated at high *pH* values, usually above 5. The *pH* is conveniently maintained by keeping a little zinc oxide suspended in the bath.

OPERATION WITH INSOLUBLE ANODES

Lead alloy¹⁷ or silicon-iron anodes may be employed. At the anode, instead of dissolving zinc, oxygen is liberated and acid is formed:



The complete reaction in the plating cell is



As zinc is plated out and acid accumulates, the cathode efficiency is lowered. The metal content is then restored by dissolving scrap zinc, zinc dust, or zinc oxide in the accumulated acid. The procedure is used chiefly for galvanizing wire and sheet steel,^{5, 6} which is discussed next.

PLATING STRIP STEEL AND WIRE

The plating of wire and strip steel presents problems different from plating formed parts. Among the more important properties of these electroplating baths are (1) fine grain structure of deposit at high current density, (2) high conductivity, (3) ease of control, (4) insensitivity to variation in both composition and impurities, and (5) high speed deposition. Throwing power becomes unimportant because the surfaces have no recesses in which zinc must be plated. The usual cyanide and acid zinc sulfate baths have been used for plating strip and wire products for many years. The Tainton process⁵ for electrowinning zinc was developed about 1930. In this process^{5, 18, 19} the zinc is obtained by leaching roasted zinc concentrates with strong sulfuric acid (33 oz/gal free sulfuric acid) that is regenerated in the plating cell. This leaching solution is purified by neutralization with the calcined zinc concentrates, filtration, zinc dust treatment, and filtration to remove the impurities. The purified electrolyte (containing 29 oz/gal of zinc sulfate) is then added to the recirculating plating cell solution. Insoluble lead-silver alloy anodes are employed. The electrolyte has a high conductivity since it contains about 33 oz/gal of free sulfuric acid. With the vigorous agitation found in electroplating wire, current densities of 1000 to 3000 amp/sq ft are used. Special polishing dies are employed to densify the plated coating.

CHLORIDE-TYPE ACID BATHS

For electroplating sheet and strip steel, several all-chloride plating baths are in use. One of these * is similar to one of the baths listed on page 446, since it contains sodium acetate as a buffer. One solution used for a sheet steel electroplating operation is of the following composition:

* Private communication from E. J. Smith, Weirton Steel Corp., Weirton, W. Va.

ZnCl ₂	18 oz/gal	(135 g/l)
NaCl	31 oz/gal	(230 g/l)
AlCl ₃ ·6H ₂ O	3 oz/gal	(22.5 g/l)
pH	3.0-4.0	

This is recognized as a modified Thompson bath.¹⁰ It is easy to control, and the bath composition is not critical. The buildup of iron in the electrolyte may become a problem by lowering the cathode current efficiency. The aluminum in the plating bath makes filtration difficult. Should it become necessary, the iron may be removed by allowing it to settle out, after zinc oxide has been added to adjust the pH.

More recent work * †,²⁰ has indicated that there are other all-chloride baths with good plating characteristics. Typical compositions of these baths are:

Bath A *

ZnCl ₂	26-32.4 oz/gal	(195-244 g/l)
NH ₄ Cl	32-38 oz/gal	(244-292 g/l)

Bath B *

ZnCl ₂	13.2 oz/gal	(100 g/l)
NH ₄ Cl	19.8 oz/gal	(150 g/l)

Bath C ²⁰

ZnCl ₂	10-20 oz/gal	(76-152 g/l)
NaCl	10-20 oz/gal	(76-152 g/l)
NaF (or F ⁻)	0.3-2.2 oz/gal	(2.3-16.6 g/l)
AlCl ₃ (or alkaline earth)	0.2 oz/gal	(1.5 g/l)
pH	4.8-5.4	

In bath A, the resistivity of the electrolyte varies from 2.5 ohm-cm at room temperature to 1.8 at 55°C. Good deposits are obtained, depending on cathode surface speed, at temperatures from room temperature to 65°C, and current densities from 100 to 1000 amp/sq ft. The preferred pH is above 3.8, so that ferric iron may be filtered out. It may vary, however, between 2 and 5. Bath B gives similar results at current densities up to 500 amp/sq ft. It has a resistivity of 2.6 ohm-cm at 55°C. Bath C is similar to the modified Thompson bath mentioned above, except that it contains fluorides. These fluorides form a complex ion with the iron in solution and prevent the alternate oxidation and reduction at the electrodes, with corresponding loss in cathode current efficiency.

* By New Jersey Zinc Company, Palmerston, Pa. (private communication from E. A. Anderson).

† By Republic Steel Corp., Cleveland, Ohio.

OPERATING CONDITIONS

The cathode current efficiency of chloride-type baths is usually 95 to 100%, and the anode current efficiency is usually in excess of 100%. In operating an acid bath in electroplating strip steel, it is apparent that there are a number of interdependent parameters. Among these are (1) strip speed, (2) current density, (3) concentration of Zn^{2+} , (4) pH , and (5) temperature. Increased strip speed permits higher current density with a given zinc ion concentration. The bath conductivity is related to pH , temperature, and concentration of conducting salts; anode and cathode current efficiencies are related to pH , temperature, and purity of anodes and electrolytes. In commercial operation it is necessary to balance these various parameters.

The principal advantages of the all-chloride bath are its high conductivity and high permissible cathode current density with high cathode speed. Both of these give lower plating costs. One of the disadvantages of chloride baths is their corrosiveness to surrounding equipment. Special precautions must be used in designing the equipment with this in mind. Another problem is the liberation of chlorine where insoluble anode connectors are used. This requires zinc anode conductors in the electrolyte, and these must be replaced periodically.

As in all acid baths, consideration must be given to the chemical solution of the zinc anodes. The anode current efficiency is usually found to be over 100%. This compares to a cathode current efficiency of 95 to 100%. A small difference between anode and cathode current efficiencies is desirable to compensate for losses of the electrolyte carried out by the plated product. Should the anode current efficiency be too high, there are several remedies which may be used. Other factors being equal, the higher the purity of the anode zinc, the lower will be the anode efficiency. In one plant, Prime Western zinc was found to be unsuitable for anodes. In general, the higher the pH of the electrolyte, the lower will be the anode current efficiency. Alloying aluminum with zinc²¹ for casting anodes has been found to reduce crystal size of the anodes and also to lower the rate of anode solution. If the anodes are left in the electrolyte continuously, the zinc-aluminum-mercury (ZAM) anodes²¹ may be found necessary. This alloy is more expensive, and its use may cause mercury spots on the product if the anodes are located above the cathode. If the cathode is not below the anodes, this alloy has been found satisfactory.

ZINC-AMMONIA BATH .

A high conductivity zinc-ammonia electroplating bath has been developed by Hubbell and Weisberg.²² This bath consists of a tetrammine salt of zinc in an excess of ammonia.* Ammonium chloride is used as a conducting salt. The bath should contain more than 10.6 oz/gal of zinc. With a moving cathode, the current density may be from 500 to 1000 amp/sq ft. Insoluble anodes are used.

The electrolyte may be prepared by leaching oxidized zinc compounds with the regenerated ammoniacal chloride or sulfate solution from the plating cell. Sally skimmings (sal-ammoniac from the hot-dip galvanizing process) and other low grade zinc-bearing materials containing chlorides, sulfates, and carbonates may be used as a source of zinc. Since this process may use these low cost sources of zinc, it is probable that it will be given more attention in the future.

SULFATE ELECTROPLATING BATHS FOR STRIP AND WIRE

All-sulfate electroplating baths have also been used in commercially plating zinc on steel wire and strip. Two typical baths follow.

	Bath A *	Bath B †
ZnSO ₄ ·7H ₂ O	50 oz/gal (380 g/l)	47 oz/gal (350 g/l)
Metallic Zn	11.5 oz/gal (87 g/l)	
Na ₂ SO ₄	9.5 oz/gal (72 g/l)	
MgSO ₄ ·7H ₂ O	8.0 oz/gal (61 g/l)	
(NH ₄) ₂ SO ₄		4 oz/gal (30 g/l)
pH	3.0-4.0	3-4.5
Temperature, °F	135-150	100-130
Current density	250-400 amp/sq ft	100-600 amp/sq ft
Voltage required	8-12 v	

* Developed by Weirton Steel Corp., Weirton, W. Va.; data in private communication by E. J. Smith.

† Developed by Republic Steel Corp., Cleveland, Ohio; data in private communication.

These baths are giving good results in commercial operation. In use, the cathode speed should exceed 100 ft/min with the higher current densities. Cathode current efficiencies are over 90%, and anode current efficiencies are approximately 100%.

* The bath is therefore not an acid bath, but is included here for the sake of completeness.

These baths are relatively non-corrosive. Insoluble anode connections (usually lead or carbon) may be used without excessive corrosion or the liberation of chlorine, found in some chloride baths. The solutions are easily purified by filtration. The principal disadvantage is their relatively low conductivity; thus high current density operation may require 12 v. It is evident that these advantages must be balanced against the higher cost of installation and operation for electrical equipment required by the use of these all-sulfate electrogalvanizing baths.

When selecting the acid plating bath to be used for plating zinc, many factors must be considered. If the cathode current density is low, the conventional zinc sulfate bath is preferable. In plating rapidly moving steel sheets, strip, or wire, the choice is between a low conductivity electrolyte, such as the sulfate type, which has good operating characteristics and is relatively non-corrosive, and a high conductivity solution, which is corrosive and presents difficulties in certain operational features. The latter class includes both the all-chloride and Tainton solutions. The present trend seems to be in favor of the less corrosive sulfate baths. It is believed that the low operating cost of high conductivity baths (all-chloride, strong sulfuric acid and zinc-ammonia) will spur research workers to find means for overcoming their disadvantages. This will become increasingly important as heavier coating weight and higher operating speeds are needed by industry.

ZINC ANODES

Three grades of zinc are in use: Prime Western spelter, often as high as 98.5% Zn; so-called "intermediate," 99.5 to 99.8% Zn; and high purity, 99.95 to 99.99% Zn. In casting, a uniform grain size is sought so that the anodes corrode evenly in the bath without forming undue quantities of sludge from undissolved zinc particles, which may give rise to rough or pitted deposits. Cloth bags are sometimes used on anodes to confine any sludge formed.

Cadmium in concentrations exceeding 0.1% reprecipitates on both anode and cathode, forming poorly conducting films on the former, and rough, pitted, semi-spongy deposits on the latter.*²³ Iron dissolves harmlessly into the solution, while lead, generally the main impurity, enters the sludge. However, large quantities of lead dissolve sufficiently to redeposit on the anode as "whiskers" and to discolor the cathode deposits.¹⁷

* Under certain conditions a Zn-Cd alloy may be plated with insoluble anodes from an acid bath. See Ref. 23.

A good intermediate grade of anode gave the following spectrographic analysis: * Pb, 0.08%; Sn, 0.002%; Cd, .08%; Cu, 0.01%; Fe, 0.01%; Mg, 0.005%; Al, trace; Zn by difference, 99.81%. Less pure anodes are satisfactory if the sludge formed during electrolysis is properly disposed of, or if the color of the electroplate is unimportant.

No difficulties are encountered with anode corrosion, except when localized neutralization of acid at the zinc surface causes a heavy crust of precipitated basic compounds of zinc, iron, lead, aluminum, and other metals; particles of metallic zinc, cadmium, copper, and lead are often included. Although anode efficiency is not impaired, the ohmic resistance cuts the current to a low value. Operating at lower pH or with better agitation of the electrolyte at the anode will prevent crust formation. Since high purity anodes are less rapidly attacked by acid, the tendency to form crusts is less noticeable. Baths containing aluminum are more troublesome than others, for film formation starts at a pH of 4.0.

Alloying additions to the anodes,²⁴ such as mercury, aluminum, magnesium, and calcium, are not necessary in sulfuric acid-zinc baths. When using a chloride bath, alloying aluminum or other metals with the zinc anodes may be found helpful in controlling high anode corrosion and the increase of zinc in the bath.

ANALYTICAL METHODS

Since acid zinc baths are not very sensitive to changes in composition, frequent analyses are unnecessary. The metal content is automatically maintained, as has already been discussed. It is generally determined with sufficient accuracy by making specific gravity readings with a hydrometer. If desired, it may be determined by ferrocyanide titration just as for cyanide-zinc baths. Chlorides may be estimated as silver chloride; and ammonium salts by decomposition with sodium hydroxide, the ammonia being taken up in standard acid, as is common practice with nickel baths. Addition agents may be determined by the use of the Hull cell.²⁵

PREPARATION OF BASIS METALS

In general, an alkaline cleaning step is used to remove oily or greasy material, followed by acid treatment of sufficient intensity and dura-

* Analysis by John Alexander, University of Wisconsin, Madison, Wis

tion to remove oxide films, with appropriate rinsing. Because acid zinc baths have no detergent properties, cleaning and rinsing must be meticulously thorough. Whereas alkaline plating baths, particularly where the cathode efficiency is low, are able to cope to some extent with residual soils on the basis metal, the acid zinc bath demands much better surface preparation.²⁶

In practice, the alkaline cleaning baths are composed of mixtures of sodium hydroxide and sodium carbonate, phosphates, and silicates; the effective agents, however, appear to be soaps formed by saponification of certain oils in the bath; of the inorganic salts, only the silicates have detergent properties of their own. Agitation of the bath is very important. It is effected by sprays, by tumbling procedures, or by gas evolved by electrolysis, that is, the so-called "electrolytic cleaning." In this process the work may be either anode or cathode, but the current density should be at least 50 amp/sq ft. The temperature for all types of cleaning should exceed 90°C. The solution may be 4 to 6 oz/gal sodium metasilicate.

Rinsing must be thorough, for fatty acid or other films precipitated from residual alkaline solution by the acid dip will either prevent zinc deposition or the deposits will be non-adherent. The acid treatment is commonly in sulfuric acid 5 to 10% by weight, at 50° to 70°C. For cold-rolled steel, about 20% by weight hydrochloric acid at room temperature is used. The time of immersion is chosen to remove the oxide on the work, and it varies from a few seconds to 15 min.

During acid treatment, hydrogen is absorbed by the steel, which accordingly may be embrittled.³ Since hydrogen does not readily diffuse out through the zinc coating, the embrittlement is not spontaneously relieved, as with more permeable coatings such as nickel. Careful studies have shown that no significant embrittlement occurs except in very sensitive steels during plating in acid zinc baths. To avoid embrittlement, therefore, the acid treatment should be kept as mild and short as possible, and hydrochloric rather than sulfuric acid should be used. Anodic pickling is sometimes employed. Inhibitors in the acid reduce embrittlement but may cause faulty adhesion of the zinc unless removed from the steel by special treatments.*

Blistering of zinc plate is the result of inadequate cleaning, but it may be aggravated by excessive hydrogen absorption. Occasionally temporary relief may be had by adding acid to the plating bath so as to produce a porous coating through which hydrogen may escape; but the trouble originates in faulty preparation of the basis metal.

* By plating in a cyanide bath, the inhibitor film is removed; but cyanide plating in itself may lead to embrittlement.

Cast iron may be pickled in weak hydrofluoric acid, but, since a state is quickly reached in which the iron will not accept a zinc coating, sand blasting or tumbling with sand and water is preferred.

With suitable preparation²⁶ adhesion of the deposit exceeding the tensile strength of zinc is obtained. Although buffing and polishing are seldom practiced, occasionally the zinc coating is given a light brushing or rolling.

TESTS OF DEPOSITS

It has been established that corrosion protection depends primarily on the thickness or weight of the deposit.^{27 29} Since protection is the purpose of zinc coating, the measurement of thickness is of first importance.

The minimum thicknesses on significant surfaces recommended by a joint committee of the American Society for Testing Materials and the American Electroplaters' Society are: "G.S." 0.025 mm (0.001 in.); "L.S." 0.013 mm (0.0005 in.); "R.S." 0.0038 mm (0.00015 in.).³⁰ Experience indicates that the "G.S." coating is adequate for general outdoor service except in certain industrial atmospheres.*³¹ The so-called "commercial" zinc coatings run about 0.008 mm (0.0003 in.). The "R.S." coatings are suitable only for indoor or temporary use.

ACCELERATED CORROSION TESTS

The widely used salt (fog) spray test⁴² has been shown²⁷ to be valueless except in comparing similar coatings, and even then minimum thickness measurements are superior. The salt (fog) spray test does not indicate performance of zinc-plated steel in rural, industrial, and other atmospheres. No satisfactory accelerated corrosion test has been devised for zinc-plated steel.

THICKNESS TESTS

The test approved by the joint committee is the microscope test.³⁰ The requirements of elaborate apparatus and exceptional skill in pol-

* The Galvanizers' Committee of the American Zinc Institute specifies 2 oz/sq ft for the best grade of hot galvanized sheet for general outdoor use. This figure includes coatings on both sides, and corresponds to an average thickness of 0.046 mm (0.0018 in.). Local thicknesses are sometimes less than half this figure.

ishing the soft zinc on hard steel have prevented general adoption of the test.

The most reliable test is the stripping test. One stripping solution has the following composition. To 100 ml of hydrochloric acid (sp. gr. 1.19) add 5 ml of a solution of 20 g of antimony oxide in 1 liter of hydrochloric acid. Zinc may also be stripped in strong, boiling sodium hydroxide. From the loss of weight and the area involved, the average coating thickness may be calculated. Variations of the test measure the hydrogen evolved, the temperature rise under standard conditions, the change in conductance of the stripping solution, or the time required for stripping.

To determine the thickness of zinc plate at a given point magnetic methods³² are employed. Dropping tests³³ are also used. Typical solutions³² consist of ammonium nitrate, 100 g/l, and nitric acid (sp. gr. 1.42), 55 g/l; or³⁴ of chromic acid, 200 g/l, and sulfuric acid, 50 g/l. Either solution is dropped at a rate of 90 to 110 drops per minute. Each second required for penetration to the steel base represents 0.000025 mm (0.00001 in.) thickness with the former solution at 23° to 27°C, and with the latter solution at 22°C. Correction tables for other temperatures are available.³⁴ The test is simple, convenient, and accurate within 20%, but often it is very difficult to see the endpoint. The copper sulfate, or Preece, test is quite misleading even when carefully controlled.³⁵⁻³⁸ It is unfortunate that the method persists in general use.

Acid zinc deposits have a gray or white color, matte finish, and occasionally some luster. Adhesion tests consist in bending the plated metal in various ways; the zinc plate should neither crack nor peel. The Brinell hardness of electroplated zinc is about 40 to 50.^{39, 40}

CYANIDE ZINC

R. R. BAIR * AND L. J. SCHUSTIK †

The cyanide electrolyte is finding an increasingly wide field of application in zinc plating because of its ability to give practically any type of deposit ranging from white matte with excellent ductility to mirror bright deposits. The matte zinc deposit is generally used where rust protection or ductility is of prime importance, whereas the bright plating baths find application on articles requiring both corrosion protection and eye appeal. The cyanide bath is versatile in producing deposits of widely varying appearance and has excellent throwing power. These factors have firmly established the high position of cyanide zinc plating in industry.

Literature references indicate that zinc was plated from a cyanide type of bath as early as 1907 by Snowden,¹ but most of the development in cyanide zinc baths has occurred since 1919. This is particularly true of the bright plating baths. Proctor² was among the first to recommend the commercial use of cyanide zinc baths, giving three formulas for specific uses. Eichstaedt³ described a solution composition for depositing a zinc-tin alloy.

One of the first authoritative investigations of cyanide zinc baths was that of Blum, Liscomb, and Carson,⁴ who developed the fundamental chemistry and gave definite recommendations for bath composition and operating conditions. Wernlund⁵ reported results of an extended study of addition agents. Horsch and Fuwa⁶ made an extensive study of throwing power and current efficiencies of zinc plating baths and concluded that the cyanide is superior to the acid bath.

Another important line of investigations concerned the study of alloy anodes for plating zinc from cyanide solutions. Mercury was the first successful alloying metal used for this purpose.⁷⁻⁹ Further investigation indicated the value of aluminum¹⁰ and magnesium and calcium¹¹ as alloy agents. Mercury, when present in zinc anodes, will also be found in zinc deposits from cyanide baths. The function of the mercury is to improve the appearance of the deposits. The alloy-

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† E. I. du Pont de Nemours & Co., Inc., Chicago, Ill.

ing of aluminum, magnesium, or calcium with zinc is performed primarily to reduce the electrochemical solubility of the zinc. These alloy anodes will operate at the same approximate efficiency as is normally obtained at the cathode.

A more recent development in cyanide zinc baths has been the introduction of several bright plating processes which give deposits having from a semi-bright luster to a brilliant surface, resembling chromium. Other recent developments are the bright dips which impart corrosion resistance to the zinc surface and greatly enhance the brightness of the deposit. Some of these dips contain chromates or chromic acid or both. These developments have resulted in wider applications for zinc plating, when appearance and excellent rust-protective qualities must be combined with freedom from stain.

Cyanide baths are now used to a limited extent for the plating of steel strip, and this application is expected to grow. Bright zinc plating from cyanide baths fills the need for a relatively low cost means of preventing corrosion on ferrous metal parts. In numerous instances, cyanide zinc plating has replaced bright cadmium plating to good advantage because of its lower cost, greater availability, and versatility. Many more metal parts are now being plated than ever before, and the properties imparted by zinc have given this metal a high place in the electroplating industry.

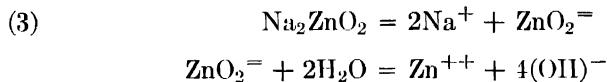
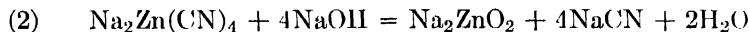
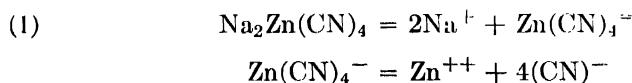
PRINCIPLES

The chemistry of cyanide zinc solutions has been discussed by a number of investigators who agree that zinc can be deposited satisfactorily from cyanide solutions only if a mixture of sodium zincate and sodium zinc cyanide complexes, with an excess of sodium cyanide or sodium hydroxide or both, is present.

Comparison of a solution of sodium zincate and sodium hydroxide with a solution of the sodium zinc cyanide complex (which must necessarily contain some sodium zincate) shows by plating tests that it is essential to have all three primary constituents present to produce consistently high grade deposits at high cathode efficiencies. From the sodium zincate bath, spongy and poor quality deposits may be obtained at high current efficiencies and at very low current densities. White, matte deposits are obtained from the sodium zinc cyanide bath at high current densities and low efficiencies. Only after sodium cyanide has been added to the zincate bath are worth-while deposits obtained at reasonably high cathode efficiencies. The functions of sodium cyanide are: (1) to combine with the zinc to form soluble com-

plexes, and (2) to provide a control method for the appearance of deposits. Current efficiency is also closely dependent on the sodium cyanide content; hence close control of the cyanide concentration is necessary in order to obtain good quality of deposit at high current efficiencies.

The exact ratio of sodium zincate to the sodium zinc cyanide complex is impossible to determine, but Hull and Wernlund¹² had indications that 75 to 90% of the zinc metal is present in the bath as sodium zincate and the balance as sodium zinc cyanide. The equilibrium is affected by the relative concentration of uncombined sodium cyanide and sodium hydroxide in the bath. Zinc ions are available in the solution from both sodium zincate and the complex sodium zinc cyanide. The following equations show the probable ionization:



These equations indicate the complexity of the cyanide zinc plating solution. The solution constituents can be controlled by analysis, so that satisfactory results can be obtained from the cyanide zinc solution. The basic constituents which require analytical control are: (1) zinc metal, (2) sodium cyanide, (3) sodium hydroxide, and (4) metallic addition agents that may be used. Whereas the first three of the above are interdependent, the most important relationship is between sodium cyanide and zinc metal.

A term used universally in expressing the composition of cyanide zinc solutions is the ratio of all CN^- present, expressed as NaCN , to the zinc metal. The total CN^- is calculated from the sum of the free sodium cyanide and the sodium cyanide equivalent of the zinc cyanide in the bath. The optimum value for this ratio is affected by the sodium hydroxide and metal concentrations. The expression of "ratio" applies to all cyanide zinc baths.

The addition of various secondary salts has been proposed for improvement of either plate quality or electrical efficiency. Sodium fluoride or aluminum salts are reported to whiten the deposits, and mercury, to a certain extent, improves throwing power and whitens the deposit. There is still a third class of metallic addition agents,

such as molybdenum and chromium,¹³⁻¹⁵ which are used primarily in conjunction with organic brighteners.

CURRENT EFFICIENCY

The following discussion indicates the effect on efficiency of varying the concentrations of the principal constituents.

METAL

Zinc, dissolved in the bath in the form of sodium zinc cyanide or sodium zincate, is the source of metal for deposition on the work. Be-

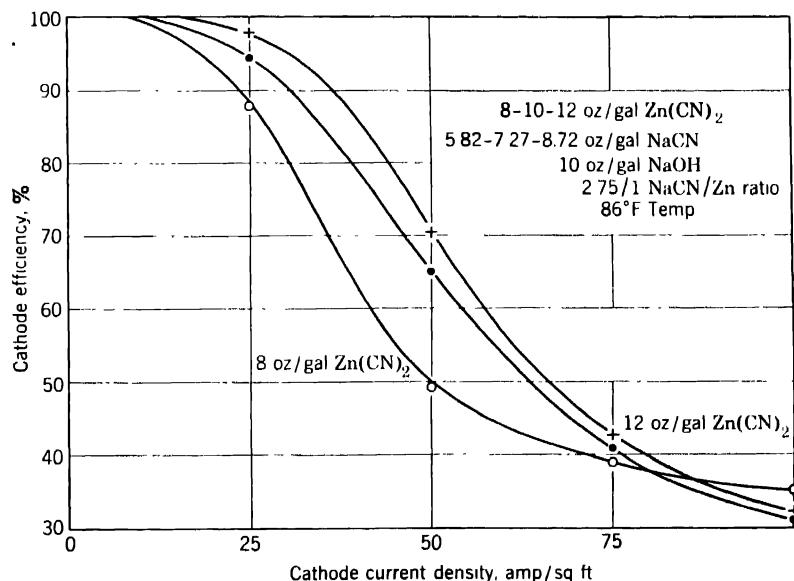


Fig. 1 Effect of metal on cathode efficiency.

cause of the dissociation of the sodium zinc cyanide or the sodium zincate complexes or both to form zinc ions, zinc can be plated from cyanide zinc solutions.

All other conditions being unchanged, the efficiency of cyanide zinc solutions increases as the metal content of the bath is increased. This results in a decrease of brightness of deposit, owing primarily to an increase in cathode efficiency. This effect can be offset by other variations in the bath or in operating conditions, as will be discussed later. The effect of metal concentration on the efficiency of a commercial cyanide zinc solution is shown in Fig. 1.

TOTAL CYANIDE

There is a definite relation between the concentrations of zinc and of total sodium cyanide for optimum results. This ratio, for most operations, covers a range of 2 to 3 of total cyanide to 1 of zinc. In general, as the ratio of total cyanide to zinc is increased, the cathode efficiency is decreased, and the deposits change from dull matte to bright. The effect of the ratio variation shown in Fig. 2 may be offset

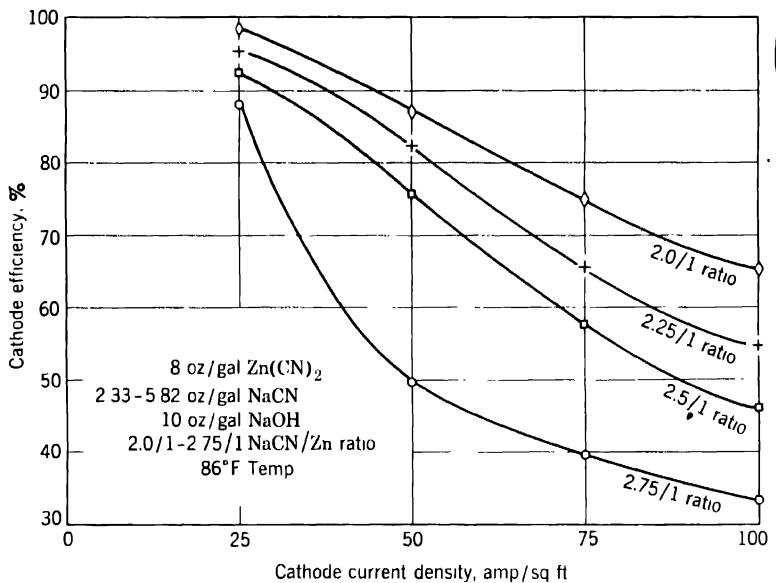


Fig. 2. Effect of ratio on cathode efficiency.

completely by variations in operating temperature or partially by variations in metal content.

CAUSTIC (SODIUM HYDROXIDE)

Cyanide zinc baths may be operated satisfactorily with a caustic range of approximately 7 to 16 oz/gal, optimum concentrations being 10 to 12. Concentrations of caustic below 7 oz/gal will cause grainy deposits at a low cathode efficiency. As the caustic content of the bath is increased and approaches 14 to 16 oz/gal, the bath conductivity is improved and the cathode efficiency is increased. The curves in Fig. 3 show the effect of increasing the caustic content on the current efficiency of a commercial bath.

High caustic concentration in the bath will increase both the chemical and the electrochemical solubility of zinc anodes. This may be

a disadvantage in certain instances, since it may result in excessive buildup of metal in the bath.

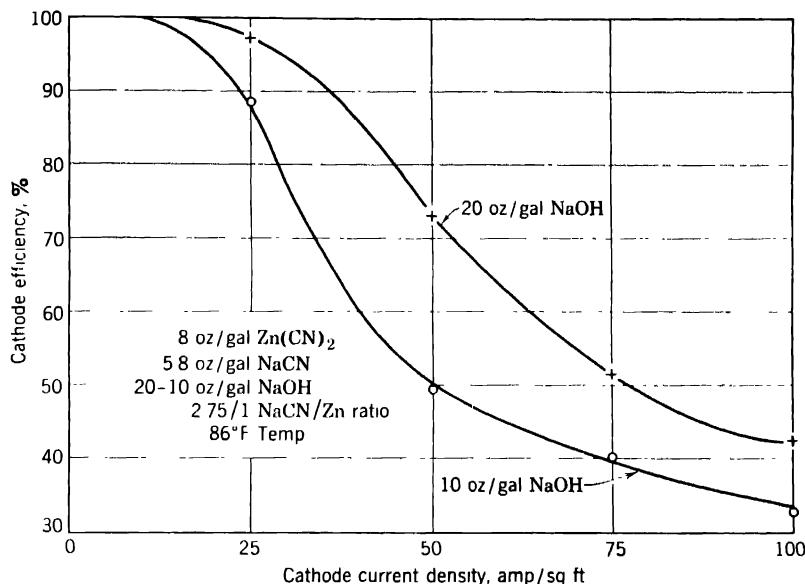


Fig. 3. Effect of caustic on cathode efficiency.

TEMPERATURE

Another set of tools useful to the zinc plater relates to variations in the operating conditions, temperature, and current density. For any given bath formulation low temperatures decrease electrical efficiency and increase deposit brightness and throwing power. The converse of this is true, i.e., high operating temperatures increase electrical efficiency and decrease the throwing power and brightness of deposit. Several of the proprietary organic brighteners are not stable at temperatures in excess of 35°C. This feature limits the operator in obtaining the maximum effect from high temperature operation. The curves in Fig. 4 show the variation of cathode efficiency versus current density at several temperatures.

CURRENT DENSITY

For any given bath composition and operating temperature, low current density deposit, such as that in recesses of irregularly shaped objects, tends to be cloudy. High current density points on the same article will be bright and will have appreciably thicker deposits. This

suggests operation at sufficiently high average current densities to be outside of the dull or hazy low current density range. Another advantage of high current density operation is the relative improvement in plate distribution or throwing power.

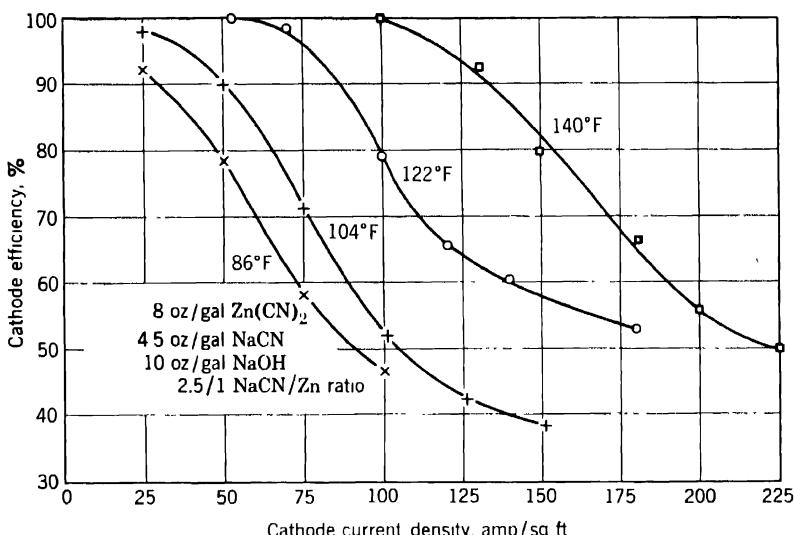


Fig. 4. Effect of temperature on cathode efficiency.

PURIFICATION

Purification of cyanide zinc solutions is required, since the presence of even traces of such metals as copper, lead, cadmium, silver, or tin will make the deposition of bright coatings very difficult, if not impossible. The removal of contaminating metals is accomplished either chemically or electrolytically or by both methods.

The required degree of purification is determined by the desired quality of deposits. Plate from an unpurified bath may be dull and dark gray. It has little eye appeal and is generally used on parts that are concealed. Deposits from an adequately purified bath are uniformly lustrous to bright, having an excellent appearance. Only *thoroughly purified* cyanide zinc solutions will produce the typical bright zinc deposits. Proprietary brighteners usually increase to a limited extent the tolerance of the solution to metallic contamination.

Metals such as cadmium and lead may be precipitated by the addition of sodium sulfide or, preferably, sodium polysulfide. The in-

soluble sulfides remain in the solution as a sludge which collects at the bottom of the tank. Because copper sulfide is soluble in the cyanide zinc solution, copper is removed by displacement with finely divided zinc dust. When a relatively large amount of contaminating copper is present, it may be necessary to repeat the zinc dust purification several times.

Electrolytic purification is used for removal of the last traces of impurities. This method also has an advantage of preferentially removing certain types of contaminants. For instance, Cr⁺⁶ may be reduced to Cr⁺³ and plated out by high current density, low efficiency electrolysis, while tin and copper may be removed effectively by low current density, high efficiency electrolysis. The electrolytic method of purification is excellent, since it introduces no inert salts and does not materially change the basic composition of the solution.

PLATING BATH FORMULAS, OPERATING CONDITIONS, AND MAINTENANCE

The formulas recommended for cyanide zinc plating baths may be divided conveniently into: (1) the conventional process, as described by Blum and Hogaboom;¹⁶ (2) the zinc-mercury process; and (3) the bright zinc processes.

CYANIDE BATH WITHOUT ADDITION AGENTS

Solution Composition	Ounces per Gallon	Grams per Liter
Zinc cyanide, Zn(CN) ₂	8	60
Sodium cyanide, NaCN	3	23
Sodium hydroxide, NaOH (caustic soda)	7	53
Operating Conditions		
Temperature	40–50°C (104°–122°F)	
Current density	9.3–19 amp/sq ft	
Cathode current efficiency	90–95%	
Anodes, high grade	99.75% + zinc	

The solution composition should be maintained within $\pm 10\%$, and the ratio of total sodium cyanide to zinc should be within the range 2.0 to 2.5 to maintain good throwing and covering power. The bath is used for production of zinc coatings primarily for rust protection

and serves admirably for this purpose. The zinc plate has good quality and high ductility.

To improve the whiteness and stain resistance of deposits from this type of bath, gum arabic with sodium fluoride and lead salt¹⁷ have been patented as additions to the bath.

The above cyanide bath without addition agents has been modified recently to permit rapid deposition, up to 125 amp/sq ft at high cathode current efficiency. The composition recommended for this purpose follows.

Solution Composition	Ounces per Gallon	Grams per Liter
Zinc cyanide, $\text{Zn}(\text{CN})_2$	12	90
Sodium cyanide, NaCN	5	37.5
Sodium hydroxide, NaOH (caustic soda)	12	90
Operating Conditions		
Temperature	104–158°F	
Current density	55–110 amp/sq ft	
Cathode current efficiency	85–95%	
Anodes, high grade	99.75% + zinc	

ZINC-MERCURY PROCESS

This process^{7, 9} depends on the production of a zinc-mercury alloy plate (0.5 to 1.0% Hg) which is smooth, white, and more pleasing in appearance than the plate from the straight cyanide bath. It compares favorably with the acid zinc process in this respect.

Solution Composition	Still		Barrel	
	oz/gal	g/l	oz/gal	g/l
Zinc cyanide, $\text{Zn}(\text{CN})_2$	5	37.5	8	60
Sodium cyanide, NaCN	3	22.5	4	30
Caustic soda, NaOH	4	30.0	6	45
Mercury salt *	0.03	0.25	0.03	0.25

Operating Conditions

Temperature	86–122°F optimum (40°C) 104°F
Anodes (intermediate or Prime Western)	98.25% Zn + 0.5–1% Hg
Anode current density	10–15 amp/sq ft
Ratio anode to cathode surface	2:1
Cathode current density	up to 40 amp/sq ft
Voltage	4–6 v at the tank
Cathode current efficiency (25 amp/sq ft)	90%
Throwing power (Haring cell)	35–40%

* Any mercuric salt such as HgCl_2 or HgO is dissolved in NaCN .

BATH MAINTENANCE AND CONTROL

For good anode corrosion, not less than 4 v must be maintained across the plating tank bus bars, and an anode current density of 10 amp/sq ft should be used. If, under normal load, the tank voltage is less than 4, anodes are removed until the desired voltage is secured.

When properly operated, the solution contains from 0.013 to 0.027 oz/gal of mercury cyanide. During weekends or other longer shutdowns, most of this mercury deposits out on the anodes (by displacement), making it necessary to replenish the mercury in the bath by adding mercury salts before operation is resumed. During electrolysis, mercury codeposits with the zinc. If the bath builds up in zinc, about one-third of the zinc anodes may be replaced by steel anodes, preferably casehardened. Under normal operation, a brown film covers the zinc anodes, and uniform corrosion is maintained. The principal precaution to insure efficient anode performance is to avoid low anode current densities or excessive mercury salts in the bath, as either may result in mercury spots in the plate.

Since the bath is "self-purifying," only intermittent filtration of the solution is required to remove ferrocyanide and other insoluble salts. As in the case of the plain cyanide bath, all bath constituents should be maintained within $\pm 10\%$ of the recommended concentrations.

The zinc-mercury bath possesses good throwing power and good covering power (ability to plate readily at low current densities). The rust-protective value of the alloy deposit is about the same as that of an unalloyed zinc deposit.

BRILLIANT PLATING BATHS

The bright plating cyanide baths were introduced in 1935 and have come into widespread use, until, at the present time, they are among the foremost methods for obtaining good corrosion protection as well as excellent eye appeal of plated ware. A factor in the widespread use of the bright plating zinc baths has been the recurring shortage of cadmium. It cannot be said that zinc will compete in all instances with cadmium, since each has its own particular fields of application. However, zinc is being more widely used than ever before. The increased use of the bright zinc processes results from their ability to give brilliant deposits directly.

There are four basic conditions that must be observed in the consistent production of satisfactory bright zinc deposits. The first of these is that the plating bath and chemicals must be virtually free

from heavy metal impurities. It is well known that minute amounts of the metals copper, lead, and cadmium affect the physical and chemical properties of zinc metal to a marked degree. This has likewise been found true in bright zinc plating.

The high degree of purity required in zinc plating solutions is maintained by using high purity zinc anodes¹⁸ and by various methods of purification of the bath. Purification agents are usually either sodium polysulfide, sodium sulfide, or zinc dust. The addition of 0.1 to 1.0 g/l (0.014 to 0.14 oz/gal) of the polysulfide or sulfide or both in the form of a concentrated solution is effective in precipitating lead and cadmium. Zinc dust, 0.25 to 2.5 g/l (0.033 to 0.33 oz/gal), is effective in removing copper. After the zinc dust is added, the bath is stirred thoroughly and filtered. The zinc dust has the additional function of reducing the valence of chromium and molybdenum which may be present in the bath so that these materials no longer cause blistering, which will occur if they are present in the high valence state.

The second condition for obtaining consistently bright deposits relates to close control of essential bath constituents; i.e., the zinc metal, caustic soda, and total cyanide contents must be maintained within certain well-defined limits. Simple methods for chemical analysis are available for this control. Addition agents used to enhance the brightness of deposits are generally controlled by plating tests. Use of the Hull cell¹⁹ is an ideal way of determining the degree of purity of the bath, the balance of the three main constituents, and the concentration of addition agents. Thus the Hull cell operation supplements the routine chemical analyses.

TABLE 1. EFFECT OF RATIO TOTAL NaCN ON BRIGHT PLATE CURRENT DENSITY Zn (METAL)

Ratio	Range and Efficiency	
	Approx. Bright Plate Current Density Range, amp/sq ft	Cathode Efficiency at 35 amp/sq ft and 85°F
2.25	37-93	92%
2.5	18-93	88%
2.7	9-93	82%
3.0	4.7-75	69%
3.2	2.8-75	54%

The third condition for bright zinc plating involves rigorous control of the ratio of total sodium cyanide to zinc. Table 1 gives the results of varying this ratio as related to bright current density range and cathode efficiency, and it shows the narrow range of ratios within which practical current densities give high current efficiencies. The ratio should be held between 2.5 and 2.7 for operation at high efficiency for normal current densities at room temperatures. The ratio is also dependent upon bath temperature, if all the operating factors are to function at their optimum value. Table 2 gives the optimum ratio for various operating temperatures.

TABLE 2. OPTIMUM RATIO VALUES VS. TEMPERATURES

Optimum Ratio	Temperature °C	Temperature °F
2.6	27.8-30.6	82-87
2.8	31.1-33.3	88-92
3.0	33.9-37.8	93-100

A fourth factor in obtaining consistently satisfactory bright zinc deposits from cyanide baths is the use of bright dips or addition agents or both. Nitric acid (0.25 to 0.50%) can be used for bright dipping and passivating the surface of zinc deposits. Recently the use of passivating dips containing chromic acid or dichromates has gained widespread popularity. The chromic acid dips give excellent results in brightening of deposits as well as imparting improved salt spray performance. The chromic acid bright dips have the disadvantage of removing appreciable amounts of zinc deposit (0.0001 to 0.0002 in.).

The proper operation of bright zinc bath depends in a large part upon the use of addition agents which are effective in one or more of several functions as follows: (1) improvement in tolerance of the bath to metallic impurities, (2) brightening effect upon deposits, (3) widening of the current density limits at which bright deposits are obtainable, and (4) permitting production of bright deposits without bright dipping.

The addition agents may be organic or inorganic in nature. In general, the organic addition agents do not plate out to become a part of the deposit at any appreciable rate. Organic addition agents usually require maintenance because of their instability or volatility. The inorganic addition agents, such as molybdic oxide,²⁰ are very stable in the bath and are removed from the bath by drag-out or by codeposition only. There are no published methods of analysis for determining the organic addition agents. Plating tests are used to determine the

necessity for replenishment. Optimum addition agent concentrations are usually different for still and for barrel plating operations. Some prepared addition agents differ in composition, depending upon the specific application. Others are effective only in barrel plating, for which the addition agent must function at the very low current densities and very high efficiencies that are obtained.

A complete understanding of the operating principles of cyanide zinc baths is more important in the operation of the bright plating baths than in the dull plating baths. Improper operation or maintenance will result in immediate loss of brightness or in low cathode efficiencies, whereas there will be no visible change in results from the dull plating baths. Decrease in the quality of work from the dull plating baths will result in a decrease in corrosion protection, caused by a change in cathode current efficiency and throwing power.

The exact solution composition used is determined by: (a) the type of deposit desired, (b) size and shape of the work, and (c) whether the installation is of a "still tank" or "barrel" type. A high ratio of total cyanide to zinc or low operating temperature or both will tend to give bright deposits. Large, irregularly shaped work indicates the advantageous use of high ratio baths at normal temperatures. Current densities of 20 to 40 amp/sq ft are normally used in still tank operations and of 2 to 10 amp/sq ft in barrel plating.

Barrel plating operations require a solution having a low current density bright range and a high conductivity. This necessitates operation of baths having higher total cyanide to metal ratios and higher caustic concentrations than would be used for still plating.

RANGES OF BATH COMPOSITION FOR BRIGHT ZINC PLATE

Solution Composition	For Still Plating		For Barrel Plating	
	oz/gal	g/l	oz/gal	g/l
Zinc cyanide, Zn(CN) ₂	8.0-11	60-82	8.0-11	60-82
Sodium cyanide, NaCN	2.5-8.5	18.7-64	4.5-10	34-75
Sodium hydroxide, NaOH (caustic soda)	10-15	75-112	10-13	75-97
Corresponding zinc metal	4.5-6.0	34-45	4.5-6.0	34-45
Corresponding total NaCN	9-18	68-135	11-19	68-135

$$\text{Ratio} = \frac{\text{total NaCN}}{\text{Zn}} = \begin{cases} 2.0-3.0 & (\text{still}) \\ .2 & (\text{barrel}) \end{cases}$$

The exact concentrations of bath constituents are not critical and may be varied quite widely, particularly if the proper relation of total sodium cyanide to zinc is maintained.

OPERATING CONDITIONS

The operating conditions for the various bright zinc processes are likewise quite similar and can be conveniently summarized as follows:

Temperature	20–45°C (68–113°F), extreme limits 28–38°C (82–100°F), preferred limits
Cathode current density	2–100 amp/sq ft, extreme limits 10–50 amp/sq ft, average limits
Tank voltage	1.5–6 v (still) 10–15 v (barrel)
Cathode current efficiency	75–95%
Throwing power (Haring cell), 5:1 ratio	35–55%
Solution conductivity	4.5–5.5 ohm-cm
Anode current density	10–30 amp/sq ft
Anodes (special high grade or high grade)	zinc ball anodes of high purity ^{21, 22} 99.8% + zinc bar anodes zinc-aluminum also with mercury, ¹⁰ zinc-calcium, or zinc-magnesium ¹¹

OPERATION AND MAINTENANCE OF BRIGHT ZINC PLATING BATHS

An important point in bright zinc plating, particularly if the deposits are to be bright dipped, is the necessity for adequate rinsing of the work after plating and after bright dipping. Optimum results require two cold water rinses before bright dipping and at least two cold water rinses and one hot water rinse after bright dipping.

In barrel plating in which as much as 5 amp/gal may be passed, cooling coils must be used to provide proper temperature control. Unless the basic formulation of the bath is modified for low temperature operation, the anodes may become polarized at temperatures below 21°C.

ZINC PLATING OPERATIONS**RACK PLATING**

When the cyanide solution is used, a 6-v source of direct current of sufficient capacity to provide between 35 and 50 amp/sq ft is required for consistent uniformity of thickness and appearance.

The following cleaning and plating cycle is in general use commercially with some slight modifications in specific instances on particular jobs.

1. Soak in hot alkaline cleaner to remove or loosen grease, oil, and drawing compounds.

2. Electrolytic clean in hot, concentrated, alkaline reverse current cleaner to remove balance of oil, grease, or drawing compound and any other organic or inorganic dirt adhering to the part.

3. Water rinse. Either a dip or a spray rinse or a combination of both with flow of water sufficient to insure complete removal of the cleaner is required.

4. Acid dip. Hydrochloric acid at room temperature in concentration of 5 to 50% by volume (of 1.18 sp. gr. acid) is used, depending on the amount of rust to be removed.

5. Water rinse as in step 3.

6. Soak in sodium cyanide solution, 4 to 6 oz/gal, at room temperature to remove any slight rusting during transfer from acid and acid rinse. Cyanide added to this tank helps maintain cyanide in the succeeding zinc plating tank.

7. Zinc plate.

8. Water rinse. This is sometimes maintained as a stagnant rinse to recover drag-out of zinc solution. It is returned to the plating tank as required to maintain the operating level of that tank.

9. Water rinse as in step 3.

10. Bright dip. Usually 0.25 to 0.5% by volume of 1.42 sp. gr. nitric acid, freshly prepared every 8 hr of operation, is used.

11. Water rinse as in step 3.

12. Hot water rinse—or drying oven.

High carbon, casehardened steel or steel which has been heavily pickled to remove scale can be plated by extending the time in a reverse current cleaner. After zinc plating, these steels are relieved of hydrogen absorbed during the plating operation by baking at 325 to 350°F for 2 to 4 hr. Absorbed hydrogen causes embrittlement of the steel and can cause blistered or spotted deposits after aging of the plated work.

Anode rods can be made of steel and submerged just below the solution level. This insures positive contact at all times and reduces the possibility of copper contamination which is always present when copper or brass rods are used. Cyanide spray crystallizes on the rods and is washed into the bath when anode rods are cleaned. Crystallization from cyanide spray can build up on anode rods so that anodes are actually held out of contact. When this happens, spongy, loosely adherent zinc deposits on these anodes owing to bipolar effect. This spongy zinc can be a source of serious roughness.

Solutions in continuous operation are maintained by additions of sodium cyanide, brightener (if used), and zinc anodes. Caustic soda is

sometimes required in small quantities to replace drag-out. Reagents to precipitate heavy metal impurities are added daily or whenever other additions are made. The sulfides and polysulfides completely remove lead and cadmium which are causes of "burning" and dark deposits. Zinc dust will remove copper as well as lead and cadmium. Copper contamination causes darkening of deposits when bright dipped in 0.25 to 0.5% nitric acid. Sodium polysulfide is generally used because it effectively removes the impurities without excessive sludge. Sodium sulfide is cheaper but produces a heavy sludge, necessitating more frequent cleaning of the plating tanks. The amount of purification required depends on the purity of the anodes used. High grade zinc anodes require $\frac{1}{60}$ oz/gal or less daily to maintain an excess of polysulfide in solution. An excess of sulfide is not detrimental and should be maintained at all times. If solutions are filtered, sulfide should be added before operations are resumed.

Stainless steel contacts can be used on insulated copper racks to eliminate copper contamination of solutions. Uninsulated racks are usually made of steel brazed on a copper hook at the solution level.

BULK PLATING

In barrel plating the parts are cleaned and handled in bulk. Most units operate with a 12- to 15-v source of direct current of sufficient capacity to produce 500 to 750 amp/barrel. Lower voltage considerably lengthens plating times required for specified thicknesses, because most of the voltage is required to overcome the resistance of the barrel. Solution composition is similar to that used in still plating except the caustic is maintained at 12 to 15 oz/gal to increase the conductivity of the bath. Cold water is piped through coils in the barrel tanks to take out the heat generated by the current flow. Coils are discharged into a rinse tank following the plating tank to obtain full use of the water.

Parts for barrel plating are usually cleaned in monel or stainless steel baskets, or are tumbled in monel or stainless steel cylinders. A typical cycle is given below:

1. Degrease in solvent-type degreaser.
2. Soak or tumble in alkaline immersion cleaner.
3. Water rinse.
4. Acid dip. Cold 5 to 10% by volume of 1.18 sp. gr. hydrochloric acid is used.
5. Water rinse.
6. Sodium cyanide dip—4 to 6 oz/gal (room temperature).

7. Load into plating cylinder and plate for required time to obtain thickness specified.
8. Water rinse.
9. Bright dip (if used).
10. Water rinse.
11. Hot water—dry.
12. Bake.

It is sometimes difficult to start deposition of zinc on high carbon or casehardened steel because of a film of hydrogen bubbles adhering to the work. This may result from overpickling of the parts or from too high a ratio of total cyanide to zinc metal. If barrels are raised out of the zinc solution, allowed to drain, and lowered again when the hydrogen has evolved from the solution, deposition usually starts immediately.

ANALYTICAL METHODS

ZINC

Reagents. Solution: exactly 33.0 g/l $K_4Fe(CN)_6 \cdot 3H_2O$ and 6 g/l Na_2SO_3 ; indicator: saturated solution of uranium acetate.

1. Under a hood, to exactly 5 ml of cyanide zinc solution in a 250-ml beaker, add 10 ml 1:1 nitric acid and 10 ml 1:1 sulfuric acid. Boil until dense white fumes are liberated and fume about 5 min more.
2. Let cool and cautiously add 50 to 75 ml distilled water, 15 g ammonium chloride and dissolve completely.
3. Make ammoniacal (to litmus), add an excess of 5 ml of concentrated ammonium hydroxide (sp. gr. 0.9015), filter, and wash the precipitate with hot distilled water containing 10 ml/l concentrated ammonium hydroxide.
4. Make the filtrate neutral to litmus with hydrochloric acid, and add 5 ml concentrated hydrochloric acid (1.18 sp. gr.).
5. Add 25 ml hydrogen sulfide saturated distilled water.
6. Bring the volume to 300 ml and heat to 80° to 85°C.
7. Titrate with potassium ferrocyanide solution, using uranium acetate on a spot plate as an outside indicator, to the first light red-brown tinge.

Number of milliliters of standard potassium ferrocyanide required divided by 5 equals ounces per gallon of zinc.

TOTAL SODIUM CYANIDE

Reagents. Solutions: exactly 13.0 g/l c.p. silver nitrate solution, 10% sodium hydroxide; indicator, 10% c.p. potassium iodide solution.

1. Dilute exactly 1 ml of plating solution sample to about 150 ml in a 250-ml Erlenmeyer flask.
2. Add 5 drops 10% potassium iodide indicator solution and 5 ml of 10% sodium hydroxide solution.
3. Titrate with silver nitrate solution, stirring constantly, to the first permanent opalescent color.

Number of milliliters of standard silver nitrate solution required equals the number of ounces per gallon of total sodium cyanide.

Note: The presence of sodium sulfide in the plating solution will obscure the endpoint through precipitation of brown or black silver sulfide. This sulfide may be removed by shaking a portion of the sample with *dry* basic lead carbonate. Then the sample is filtered, using a *dry* filter. The filtrate may then be sampled and analyzed.

SODIUM HYDROXIDE (CAUSTIC SODA)

Reagents. Solution, 0.940 *N* sulfuric acid; indicator, LaMotte sulfo-orange solution.

1. To exactly 5 ml of plating solution in a 250-ml Erlenmeyer flask, add 1 g of NaCN, 10 ml of water, and 10 drops of indicator solution.
2. Titrate with the standard sulfuric acid solution to a color change from orange to yellow.

Number of milliliters of standard sulfuric acid required equals number of ounces per gallon of caustic soda.

SODIUM CARBONATE

Reagents. Solutions, barium chloride (10%), hydrochloric acid (0.710 *N*) ; indicator, methyl orange-xylene cyanole indicator solution.

1. In a 250-ml Erlenmeyer flask dilute exactly 5 ml of plating solution to about 100 ml with hot distilled water.
2. Add 15 ml of barium chloride solution, heat to boiling, and allow to settle on the steam plate for 30 min after closing the mouth of the flask with a wad of cotton.
3. Filter through No. 41 Whatman Paper, washing the flask and the residue on the paper with hot distilled water.
4. Return the paper and precipitate to the original flask, add 100 ml of hot distilled water, 3 drops of methyl orange-xylene cyanole, and shake to pulp the paper.
5. Titrate with standard hydrochloric acid to the first permanent color change of green to purple.

Number of milliliters of standard hydrochloric acid solution required equals number of ounces per gallon of sodium carbonate.

MOLYBDENUM

Reagents. Solutions, potassium permanganate (0.117 *N*) ; saturated solution of ferric alum, 2 parts by volume + phosphoric acid (c.p. 85%, sp. gr. 1.69) 1 part by volume. Jones reductor (see Scott's Analysis, Vol. I, or Treadwell and Hall, Vol. II, for description).

1. Under a hood, to exactly 5 ml of zinc solution in a 250-ml beaker, add 10 ml 1:1 nitric acid and 10 ml 1:1 sulfuric acid. Boil until dense white fumes are liberated and fume about 5 min more.

2. Let cool and cautiously add 50 to 75 ml distilled water, dissolving the precipitate completely.

3. Make ammoniaal (to litmus), add an excess of 5 ml concentrated ammonium hydroxide, filter, and wash precipitate with hot distilled water containing 10 ml/l concentrated ammonium hydroxide (sp. gr. .9015).

4. Make filtrate acid to litmus with sulfuric acid; add 2 to 3 ml concentrated sulfuric acid (sp. gr. 1.84) in excess. Pass slowly through the Jones reductor into 15 ml of the ferric alum-phosphoric acid solution diluted with 100 ml of distilled water. *Caution:* (1) Be sure the tip of the reductor tube extends below the surface of the ferric alum-phosphoric acid solution. (2) A blank sample should be run when a new potassium permanganate solution is used.

5. Wash the reductor with 100 ml of 2.5% (by volume) sulfuric acid solution and titrate with potassium permanganate solution to a permanent faint pink.

Number of milliliters of standard potassium permanganate solution divided by 10 equals number of ounces per gallon of molybdenum.

MERCURY IN SOLUTION

Reagents. Solution, potassium iodide (8.300 g/l); indicator, KNO_2 (c.p.), starch 1% (freshly prepared solution).

1. Under a hood, acidify to litmus exactly 50 ml of plating solution in a 250-ml beaker with nitric acid (sp. gr. 1.42), and boil until all cyanides are removed. Cool.

2. Neutralize with ammonium hydroxide to litmus, then add 2 ml concentrated nitric acid (sp. gr. 1.42).

3. Cool to 20°C and add a small crystal of KNO_2 .

4. Slowly titrate with standard potassium iodide solution, using 1% starch solution on a spot plate as an outside indicator, to a deep blue color.

Number of milliliters of standard potassium iodide solution required

minus 0.5 ml (correction factor for a blank) times 0.0134 equals number of ounces per gallon of mercury.

ANODES

The type of anodes used for cyanide zinc plating varies quite widely and depends on the type of bath and kind of operation. The required quality of deposit indicates the grade of zinc to be used as anode material. The two main forms are the common bar type and the ball or similar basket-contained type, cast from a suitable grade of slab zinc or from a specially formulated zinc alloy.

Either the Intermediate or the Prime Western grade of zinc alloyed with 0.5 to 1% mercury⁷⁻⁹ may be used for the zinc mercury process. These same grades of zinc were formerly used quite extensively in cyanide zinc plating for general rustproofing operations.

With the advent of the bright plating baths, which require practically complete freedom from heavy metal contaminants to obtain optimum results, the Special High Grade and High Grade high purity anodes came into general use. Even with the use of high-purity anodes it is usually necessary to purify the bath frequently, if high quality deposits are to be produced consistently.

If alloys are used in which metals such as aluminum, calcium, or magnesium²³⁻²⁵ (which have no contamination effect) are present, the character of the zinc deposit is not influenced adversely. The alloy metals may be advantageous in improving the corrosion characteristics of the anodes. Zinc passes into solution by both electrochemical and chemical attack; hence it usually tends to accumulate in the bath to an excessive degree. Aluminum, when present in zinc anodes, increases the rate of anode corrosion, whereas mercury together with aluminum alloyed with the zinc tends to reduce the chemical attack and to improve anode corrosion characteristics. Magnesium or calcium alloyed with zinc is effective in reducing anode efficiency to predetermined values. For this purpose 0.18% magnesium is used in zinc anodes for still plating and 0.05% magnesium for barrel plating to reduce the anode efficiency to about 88%, which is about equal to the average cathode efficiency.

With other than specific alloy anodes, the zinc content of the bath can be controlled, although with difficulty, by using from 25 to 50% casehardened or stainless steel anodes in the tank. However, this scheme results in a serious complication: when the zinc and iron anodes remain in the alkaline solution, they produce an electrolytic

or voltaic couple and consequent dissolution of the zinc when the bath is idle. If zinc anodes do not corrode fast enough under steady operating conditions, it is common practice to use a few steel anodes, e.g., 5 to 10% of the effective zinc anode surface, to accelerate chemical attack.

PHYSICAL CHARACTERISTICS OF DEPOSITS

Zinc electrodeposits from cyanide baths may be varied from the very ductile, white crystalline type to a fairly hard, bright deposit depending on the selection of bath formulation, operating conditions, and addition agents. All types of zinc electrodeposits, whether dull white and ductile or bright and less ductile, appear to be dense and relatively free from porosity. Very coarse-grained deposits, such as are normally obtained from plain acid zinc baths, are rarely obtained from cyanide baths. Sufficient ductility of deposit may be obtained from the warm, concentrated, low ratio bath to permit the use of this type of zinc deposit in rather severe drawing operation.

TESTS OF DEPOSITS

Numerous tests have been developed for determining the thickness or corrosion resistance or both of electrodeposited zinc. The thickness tests are particularly valuable since, through their use, minimum thicknesses may be determined rather than average thicknesses such as are obtained by the ampere-minutes-per-square-foot method. Salt spray testing gives only an approximation of the corrosion resistance and expected life of zinc coatings. The Farnsworth-Hocker²⁶ intermittent immersion test, in which ammonium chloride solution is used and then the part is allowed to dry in air between each dip, is not sufficiently rapid for shop control purposes.

The Brenner magnetic test²⁷ is non-destructive and may be utilized for determining the thickness of zinc over steel.

The "dropping test" has come into rather widespread use in recent years. As originally proposed by Clark,²⁸ a solution of iodine in potassium iodide was used. This test was later modified by Hull and Strausser,²⁹ who recommended a solution of 100 g/l ammonium nitrate and 55 ml/l of nitric acid (c.p., sp. gr. 1.42). This solution is dropped at the rate of 100 + 10 drops per minute on the specimen until the base metal appears. An indicator solution consisting of 300 g/l potassium ferrocyanide (K_3FeCN_6) is sometimes used. A 1% (by volume) addition of the indicator solution is made to the drop-testing solution.

The rate of stripping is 10 sec for each 0.0001 in. of zinc. A dropping test solution as proposed more recently by Brenner³⁰ consists of 200 g/l chromic acid and 50 g/l sulfuric acid which is dropped at the rate of 100 ± 5 drops per minute. This test is quite sensitive to temperature variation and should be used as follows:

Temperature	Rate of Penetration per 10 Sec
21°C (70°F)	0.000098 in.
28°C (82°F)	0.00011 in.
35°C (95°F)	0.00012 in.

Salt spray testing of zinc deposits has increased greatly since the advent of the chromic acid type of passivating dips. These dips form a coating consisting primarily of zinc chromate, and they greatly add to the salt spray life of zinc coatings. However, the salt spray is merely an empirical test method and does not give a true indication of the performance of the passivated zinc surface in actual service conditions. This may be due in part to the variations in operation of the salt spray equipment.

18.

Uncommon Metals

FREDERICK A. LOWENHEIM *

There are many metals which are not being, or cannot be, practically electrodeposited at present. Of the 92 elements in the periodic table (pre-atomic fission), all but 19 are metals, and of these 73 only about 16 are of present importance to the electroplater. It is the purpose of this chapter to present a review of the work which has been published concerning some of the remaining 57 elements. No attempt is made to predict which of these now unfamiliar metals is most likely to win commercial acceptance as a coating.^{70, 184}

Somewhat arbitrarily, these uncommon metals may be divided into four categories. First, some are truly rare and so expensive as to make their employment quite impractical. Such a situation is always subject to change by discovery of new sources or a new process of concentration.

Second, several have not been successfully plated in spite of repeated attempts; presumably they would be used if a practical process were developed. Considerable effort has been expended, for example, on tungsten plating. It may be recalled that chromium too would have been in this class before about 1925.

Third are those metals which in all probability cannot be deposited from aqueous solutions; this class includes the alkali and alkaline-earth metals, aluminum, and beryllium. Some of these can be plated from non-aqueous solutions; although the practical objections to such electrolytes are formidable, it cannot be said that they are insuperable.³ The review by Audrieth and Nelson^{13A} may be consulted for general information on the electrolysis of non-aqueous solutions.

Fourth, there are several metals which can be readily plated and which are not notably expensive or scarce, but which nevertheless are not made use of. Such, for example, are antimony, arsenic, and bismuth. It may be assumed that the reasons for the neglect of such

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metals lie in the specific properties of the deposits: they may be mechanically unsatisfactory, or may not fill any particular need. Changing requirements or further investigation may of course alter such a situation at any time.

This chapter is essentially a review of the literature, in which every effort has been made to make the bibliography as complete as possible. It is necessary to insert a warning of one difficulty against which the searcher must be on guard: the question of how much credence should be placed in published reports of success in plating some of the "hard-to-plate" metals. Too often the authors of such reports rely on the mere appearance of a deposit at the cathode, and offer no evidence in corroboration, such as analyses of the deposit. It is more than likely that many of these deposits have in reality consisted entirely or in part of iron, entering the bath as an impurity in the reagents, or of platinum which is widely used as anode in preliminary experiments. Confirmation and checking of much of this work is sadly lacking in the literature, and more often than not attempts to repeat reported results have ended in failure.

The scope of this review has been intentionally limited by the exclusion of some fields of investigation. Electrodeposition from fused salt baths is not considered; nor is plating from the gas phase.^{177, 250} The platinum group metals are omitted. Deposition from organic solvents is included under the metals to which it applies. Many of the metals here considered have been deposited in the form of alloys, and, although mention of such work is made, reference should also be had to Chapter 3.

The arrangement here is alphabetical. Although not, perhaps, so logical as the periodic arrangement, it is felt that it will facilitate reference.

ACTINIUM

This rare radioactive element can be deposited from ethyl alcohol-acetone mixtures, using a silver anode.⁵⁹

ALUMINUM

Attempts to deposit aluminum from aqueous solution have been reported for over ninety years, but there is no convincing evidence that they have met with any success. Wöhler³⁰³ and Deville⁶⁷ failed to obtain deposits; but in 1855 Thomas and Tilley were granted a patent²⁸⁸ on the deposition of aluminum from an electrolyte prepared by dissolving freshly precipitated aluminum hydroxide or alum in a

solution of KCN. Corbelli⁵⁸ claimed a process involving the electrolysis of a solution of alum + CaCl₂ or NaCl. Gore¹⁰⁰ described several solutions, and Bertrand²¹ and Ball¹¹ others. More than twenty patents on aluminum plating were granted before 1900.²⁰⁵

Wöhler³⁰³ and Deville⁶⁷ challenged the accuracy of several of the published reports, as did Nickles,²³³ Fischer,⁸⁹ and Mierzinsky.²²¹ Others reported their failure to obtain deposits.^{120, 282, 297, 302}

More modern claims to aluminum plating have included these: Tucker and Thomsen²⁹⁰ used a rapidly rotating cathode (15,000 rpm) when the solution of AlCl₃ was so concentrated as to be a paste, at c.d.'s up to 2 amp/sq cm. Marino¹⁹¹ patented an electrolyte prepared by dissolving aluminum anodically in a strong solution of sodium pyrophosphate, phosphoric acid, and sulfanilic acid. Marino et al.¹⁹³ dissolved the "tartrate, paratartrate or oxalate of aluminum" in aqueous ammonia.

Tumanov⁹⁸ disclosed a method of preventing the re-solution of the aluminum deposited; Cowper-Coles⁶¹ said a saturated solution of sodium aluminate gave a thin deposit of aluminum. Koehler¹⁰⁸ recommended a dilute solution of AlCl₃ slightly acid with HCl at high c.d.

Fink⁷⁹ and Fink and Jones⁸⁶ claimed aluminum deposition from: 150 g/l Na₂Al₂O₄, 75 g/l dextrose, 30 g/l NaOH or 40 g/l Na₂CO₃ at 80°C.

There is no independent evidence in the literature to suggest that any of the foregoing methods are operative: see the introductory remarks in this chapter. Langbein and Brannt¹⁷⁹ discounted all reports of the deposition of aluminum from aqueous solutions.

Organic or non-aqueous solvents have been more fruitful of results. The earliest work in this line was apparently that of Plotnikov,²⁵⁴ who found that, when a solution of AlBr₃ in ethyl bromide is electrolyzed between carbon electrodes, aluminum is deposited at the cathode. Patten²⁴⁴ confirmed this, using platinum electrodes.

Many other organic solvents have been tried, with varying degrees of success: toluene, xylene, acetonitrile,¹⁷⁰ ether^{162 164} in which the aluminum is dissolved in the form of a Grignard-type compound such as diethyl aluminum iodide or ethyl aluminum di-iodide; glycerol or acetone,¹⁶⁵ benzene,^{256, 268} ethanolamine,⁶⁹ "Cellosolve,"¹⁶ mixtures of ethyl bromide, benzene, and xylene;²²³ high boiling alcohols such as glycerol or the glycols;²²³ tetra-alkyl ammonium bromides;¹⁶¹ and ethyl alcohol.⁷⁷ Inorganic solvents include liquid ammonia^{83, 286, 310} and anhydrous sulfuric acid.³⁰¹ Pyridine,²²⁸ acetamide,¹⁶ and formamide²⁹ were found unsuitable, but alloys of aluminum with iron and

zinc were deposited from the last; these deposits had no protective value.

Better documented are reports of aluminum deposition by Mathers and Blue.^{30, 196, 197} Al or AlBr₃ is dissolved in ethyl bromide-benzene mixtures; with aluminum anodes and cathode c.d. of about 8 amp/sq ft and 3 v, aluminum is deposited on copper, zinc, or steel at 68% efficiency. There is at least one report of this process being checked independently.⁸ Similar baths have been investigated by others.

Wier and Hurley^{147, 117A, 300} claim the deposition of aluminum from substituted alkyl pyridinium chlorides or bromides, or mixtures of them with benzene, in which aluminum chloride is dissolved. Their process, improved by the addition of methyl-*t*-butyl ether, was used by Safranek, Schickner, and Faust^{260A} to electroform aluminum wave guides, with satisfactory results. More recently Couch and Brenner^{59A} have disclosed an ethereal solution containing aluminum chloride and lithium hydride which is claimed to yield satisfactory thick deposits of aluminum. Murphy^{228A} has published a literature survey on the subject of aluminum deposition; and an extensive bibliography is offered in Ref. 269A.

ANTIMONY

Antimony is relatively easily electroplated from aqueous solutions: Langbein and Brann¹⁷⁹ give several formulas, none of which, however, is a truly practical electroplating bath. A peculiarity of antimony deposits is a so-called explosive form which detonates when struck. This type of plate was obtained whenever the bath contained appreciable quantities of chloride ion, and it was found that the deposits all included significant amounts of chlorine. Deposits from chloride-free electrolytes are not explosive,^{54, 55, 105, 179, 241, 283} and the c.d. may also be a factor.¹⁰²

Antimony has been deposited from baths containing tartrates, to which it is added as potassium antimonyl tartrate, the tartar emetic of commerce (Refs. 51, 100, 178, 192, 193, 198, 285, 252); fluorides (Refs. 23, 25, 27, 130, 194, 195, 199, 237, 267); fluoborates or fluosilicates (Refs. 167, 292); sulfate-cyanide mixtures (Ref. 146); and sulfides, in which the antimony is present as thioantimonite or thioantimonate ion (Refs. 26, 48, 49, 51, 63, 72, 111, 114, 149, 169, 179, 224, 253, 270, 292, 306).

The sulfide solutions have been studied more particularly in connection with the electrorefining or electrowinning of antimony; in contrast with its electroplating, these are practical commercial proc-

esses.^{6, 126, 132} Fluoride-sulfate solutions have also been studied in this connection.²⁷³

Principal interest appears to have centered in fluoride electrolytes, typified by that of Mathers, Means, and Richard,¹⁰⁹ which utilizes aloin or resorcinol as addition agent. An earlier process of Betts^{23, 25} and a recent one of Bloom^{27, 41A} are similar in that all use antimony fluoride, SbF_3 , as the basic constituent. Bloom's patents lay considerable stress on the necessity of etching the basis metal in order to secure satisfactory adhesion of the deposit. Addition agents have been claimed to improve the deposit.^{45A}

Several have pointed out^{26, 27, 41A, 190} that the general properties of antimony should make it attractive to platers; it is, in addition, relatively inexpensive and has a high electrochemical equivalent. Its neglect by platers may be laid to two factors: no really satisfactory plating bath has been developed, and the deposits have in all cases been too brittle for practical application.* Whether this is an inherent property of antimony or whether under certain circumstances ductile deposits can be obtained is an unanswered question. Deposits from citrate baths are claimed to be ductile and to retain this ductility on aging.^{281A} Superimposition of alternating current is claimed to improve plating from chloride and sulfide baths.^{51A}

Norwitz^{237A} suggests a sulfate-chloride bath containing hydroxylamine hydrochloride; and Arent^{8A} deposits antimony on steel by immersion.

The deposition of antimony from non-aqueous solutions has been studied.^{33, 110, 175, 210, 273A} Its electrochemical behavior has been the subject of considerable theoretical investigation because of the quondam importance of the antimony electrode as a pH-measuring device.

The deposition of antimony alloys has also received considerable attention (Refs. 9, 19, 32, 61A, 62, 71, 174, 192, 193, 224, 232, 262A, 264, 271, 285).

Antimony is relatively tarnish-resistant, pleasing in appearance when polished, and cheap. Its brittleness appears to be the major bar to its acceptance in the plating field.

ARSENIC

The electrodeposition of arsenic is practiced commercially, though not extensively, as a means of producing a black or gray finish, particu-

* The process of Bloom is recent, and there have been no independent reports as to whether it provides an exception to this statement.

larly for antique effects. Formulas are given in most of the standard handbooks: Langbein and Brannt¹⁷⁹ offer no less than eight, of which the two here given are deemed to be typical.

Acid solution: HCl 1 l, As₂O₃ 48 g.

Alkaline solution: As₂O₃ 1 lb, NaOH 1 lb, NaCN ½ oz, water to 1 gal.

A cyanide bath using superimposed A.C. has been described.^{51A, 51B}

The barrel plating of arsenic has been discussed;²⁴⁸ its deposition for analytical purposes has been studied, as has its electrowinning.²¹⁶ Some work has appeared on the deposition of arsenic from non-aqueous solutions; solvents studied include ether,¹⁷⁵ nitrobenzene,²¹⁰ glacial acetic acid,²⁸⁴ acetic anhydride,^{273A} liquid ammonia,³³ and acetone.²⁴¹ Presence of NaCl or KCl is said to be beneficial.²⁶⁶

BERYLLIUM

The deposition of beryllium from liquid ammonia has been patented^{35, 44} and discussed.^{33, 34, 144} Acetamide has also been used.⁶⁹ Fused alkylpyridinium halides were not satisfactory solvents for the deposition of beryllium.^{147A}

It seems unlikely that beryllium can be deposited from aqueous solutions, and failure has been reported. Nevertheless, a patent was granted for the deposition of "thin layers" of beryllium and other metals from strongly alkaline solutions saturated with the metal hydroxide.²⁶⁸ For additional bibliography see Ref. 269A.

BISMUTH

Several apparently satisfactory processes for the electrodeposition of bismuth have been reported, and it is likely that if there were any particular demand for bismuth plating it could be done. The metal is somewhat expensive in view of its lack of outstanding properties, and there do not appear to be any uses for bismuth platings.*

Solutions recommended include methyl-sulfuric acid,^{24, 219} chlorides,^{22, 47, 157, 210} nitrate + acetate,^{21, 218} nitric acid or nitric + sulfuric acid,^{22, 47, 157} strongly alkaline lyes,²⁵⁸ nitrate + tartrate,¹⁸⁶ fluosilicates,³ and sulfides.^{278, 313}

Kern and Jones¹⁶⁰ recommended a solution of BiCl₃ containing NaCl, CaCl₂, or MgCl₂, with pyrogallol or resorcinol as addition agent. Harbaugh and Mathers¹²² preferred a perchlorate bath, containing 40 g/l of bismuth oxide, Bi₂O₃, 104 g/l HClO₄, and 0.03% glue and

* At least so far as the published literature is concerned.

0.08% cresol. Piontelli²⁴⁹ concluded that the chloride baths were most economical for bismuth refining but that perchlorate solutions were preferable in plating. Vozdvishenskii et al.²⁹⁴ reported good deposits from solutions of bismuth nitrate, and further claimed that the platings had good resistance to many corrosive agents; the polished plates "resembled nickel." Levin¹⁸¹ recommends NaBiCl_4 , excess HCl and glue. Mathers¹⁹⁵ said that deposits from acidified halide baths contained large amounts (from 7 to 11%) of the halogen; in this respect the metal would resemble antimony deposited from a chloride bath. Superimposed A.C. is claimed to improve deposits.^{51A} Electrophoretic deposition of bismuth has been proposed.^{157B}

Several theoretical studies of bismuth deposition have been made.^{36, 52B, 74, 94, 250, 262A} Fink and Gray⁸⁵ studied the codeposition of bismuth and lead from a perchlorate bath. Non-aqueous solvents have also been investigated: Stillwell and Audrieth²⁸⁴ reported bright deposits from glacial acetic acid; Patten and Mott²¹⁵ obtained plates from solutions of BiCl_3 in acetone; and Plotnikov and Gorenbein²⁵⁵ electrolyzed a solution of BiBr_3 in nitrobenzene. Bismuth deposits satisfactorily from solutions in fused alkylpyridinium halides.^{147A} Booth and Merlub-Sobel³³ failed to get a deposit of bismuth from anhydrous ammonia.

CALCIUM

The deposition of calcium from pyridine solutions has been reported.²²⁸ According to Ephraim^{72A} calcium can be deposited from aqueous solutions of its chloride if methyl alcohol is added.

CERIUM

Attempts to deposit cerium from water solutions have given negative results,¹⁶² but it has been reported plated from pyridine²²⁸ and from isoamyl alcohol,¹² the latter at very low efficiency. Atanasiu and Babor,¹² using a zinc cathode, obtained a Ce-Zn alloy from a solution of CeCl_3 in methyl alcohol, at an efficiency of about 10%. Amalgams have been prepared electrolytically.^{280A} It is claimed that alternating current superimposed on direct current aids deposition, though no examples are given.^{51A} Hurley and Wier^{117A} could not deposit cerium from solutions in fused alkylpyridinium halides.

COLUMBIUM

See Niobium.

GALLIUM

Gallium is easily electrodeposited from alkaline solutions^{46A, 96, 97, 144, 206, 291} except in the presence of nitrates. If the electrolyte is cooled, the metal appears as trees; if not, as liquid globules.

GERMANIUM

Germanium can be deposited from alkaline solutions containing organic radicals such as oxalate, tartrate, etc.^{110, 144, 274} A recent report by Fink and Dokras⁸³ indicates that glycol solutions of GeI_4 give deposits; the authors also studied the deposition of germanium alloys.

HAFNIUM

The chemistry of hafnium is so similar to that of zirconium that presumably a successful method for plating the latter would apply. Specific references to hafnium deposition are therefore rare, but one Japanese patent^{171D} claims the use of aqueous solutions of oxalates or salicylates. The value of such a disclosure is doubtful, to say the least.

LANTHANUM

The deposition of lanthanum from some organic solvents has been studied.¹³ See also Ref. 51A.

MAGNESIUM

No practical method has been reported for the electrodeposition of magnesium.²⁰³ In 1884 a British patent was granted for the deposition of magnesium or its alloys from aqueous solutions containing sulfates, cyanide, and ammonium carbonate,⁹⁹ and in 1890 a German patent claimed magnesium plating from aqueous organic acids,²⁰³ while as early as 1831 Becquerel reported obtaining magnesium from concentrated solutions of MgCl_2 . These claims are certainly wrong. Some success has rewarded efforts to plate the metal from non-aqueous solvents, but the processes have not proved practical. Overcash and Mathers²³⁹ used a solution of a Grignard-type compound in dimethyl aniline, and ether solutions of similar compounds have been employed.^{75, 100A} Broughall⁴⁴ used a halide, nitrate, cyanide or thiocya-

nate in liquid ammonia; and Müller and co-workers²²⁸ MgBr₂ in pyridine. A few additional references may be cited: 7, 69, 289, 296.

MANGANESE

The electrodeposition of manganese has been extensively studied, particularly in recent years. Most of these investigations have been concerned with the electrometallurgy of low grade ores and have had as their object the electrowinning rather than the electroplating of the metal. Electrolytic manganese is an accepted article of commerce;²⁰² conditions for successful deposition, using for the most part sulfate solutions in a diaphragm cell, have been well developed, especially by the U. S. Bureau of Mines (Refs. 2, 57, 76, 121, 152, 153, 172, 189, 218, 236, 272, 277, 295, 307; this bibliography is not exhaustive).

If demand warranted, it would appear that the deposition of manganese for plating purposes could be developed without undue difficulty. Good deposits have been reported on iron, aluminum, copper, brass, and bronze, from sulfate solutions²⁸⁷ at c.d.'s ranging from 25 to 240 amp/sq ft.¹⁰⁸ Bradt and co-workers also investigated chloride solutions^{40, 248} and reviewed earlier work; they also studied perchlorates, tannates (which yielded no deposits), and a number of organic radicals of which the best was benzoate;⁴¹ but they concluded, in agreement with most other investigators, that sulfate solutions were best;³⁹ although the addition of NH₄Cl has been claimed to afford more ductile deposits.¹¹³ A typical satisfactory formula as given by Bradt and Oaks³⁰ is: MnSO₄·2H₂O, 100 g/l; (NH₄)₂SO₄, 75 g/l; NH₄CNS, 60 g/l; cathode c.d., 240 amp/sq ft; pH, 4.0 to 5.5; temperature, 25°C.

Thick deposits gave satisfactory protection.⁵⁴ Fink and Kolodney^{88, 260A} recommended a somewhat similar bath with 50 ml/l glycerin in place of the NH₄CNS, pH 2.5 to 3.0, and cathode c.d. 90 to 110 amp/sq ft. Codeposition of manganese with iron or zinc was also reported. The deposits darkened immediately on exposure to air, but this could be prevented by a chromate dip. Another variation calls for (NH₄)₂S as addition agent, with cathode c.d. 20 amp/sq ft and insoluble anodes.⁴ A study of the theory of manganese deposition has been published by Perce.^{247A} Deposition of alloys of manganese with nickel,^{112A} cobalt, iron,^{1A} and zinc has been carried out by electrolysis of sulfate solutions at room temperature, and it is reported that, the lower the manganese content, the better the efficiency; the nickel-manganese alloys are claimed to have good corrosion resistance.¹ The subject has been reviewed by Seymour.²⁷⁶

Non-aqueous solutions have been studied: pyridine solutions of $MnCl_2$ gave no deposit,²²⁸ nor did solutions in fused alkylpyridinium halides,^{147A} but acetone proved to be a satisfactory solvent⁶⁹ and liquid ammonia solutions of $Mn(CNS)_2$ yielded deposits.³³

MERCURY

The immersion plating of mercury, as an undercoat for silver plating, has been employed industrially, as a so-called "blue-" or "quicken-

dip."^{141A} According to a British patent⁴³ electrodeposition is better for this purpose than immersion plating because the hydrogen evolution prevents the formation of mercuric oxide. The bath is: $HgCl_2$, 1.5 oz; $NaCN$, 4 oz; NH_4Cl , 2 oz; water, 1 gal. In a recent patent mercury is given as one example of metals which can be deposited from hydroxythiol baths.²⁷⁹

The deposition of mercury as an analytical procedure has been extensively studied.^{90, 95, 201, 265, 296} Cyanide baths have been studied by Esin and Altymova.⁷³ Mercury can be deposited from liquid ammonia.^{33, 310}

MOLYBDENUM

The results of the extensive work which has appeared on the electrodeposition of molybdenum remain doubtful; several authors report their inability to check previous reports. According to Fink²⁶¹ molybdenum exhibits the phenomenon of "self-polarization," i.e., it will not deposit on itself, so that, as soon as a monatomic layer is formed, deposition ceases unless depolarization comes about through simultaneous deposition of another metal, or by the formation of an alloy with the cathode. Thus it can be deposited on, or into, a mercury cathode.^{78, 217, 229, 269} Claims for the plating of molybdenum are, however, fairly numerous; they include several patents;^{84, 222, 246, 258, 261, 308} but Belyaev and Lipovetskaya²⁰ were unable to confirm Paul's method,²⁴⁶ and Price and Brown²⁶¹ could not deposit molybdenum by following Yntema's directions.³⁰⁸

A "black molybdenum" plating process has been described.¹²⁹ This deposit is not metallic molybdenum but a mixture of nickel and molybdenum oxides. The bath is: 4 to 5 oz/gal ammonium molybdate, 3.5 oz/gal nickel sulfate, pH 4.3 to 4.7, temperature 55° to 80°C, c.d. 2 to 5 amp/sq ft; plating time 8 to 10 min, with agitation. After a thickness of 0.001 in. has been attained, deposition slows down and finally ceases altogether. The literature on molybdenum plating

has been reviewed and some new data offered by Ksycki and Yntema.^{174A} Good deposits of metallic Mo were claimed by these authors from various baths, containing formates, acetates, propionates, or fluorides of Na, K or ammonium. Cathode efficiencies were less than 1%.

A method of plating molybdenum-cobalt alloys has recently been patented.³⁰⁹ The bath is highly alkaline and contains Na_2MoO_4 , CoSO_4 , NaOH , Na_2CO_3 , and dextrose. The plates are claimed to be hard, bright, and adherent, but the molybdenum content is not stated. The current density is up to 5 amp/sq ft. The patent also offers a possible explanation of the function of the cobalt (or iron) in allowing deposition of molybdenum to proceed.

Several publications on molybdenum and molybdenum alloy plating have appeared very recently. Yntema and his co-workers described^{171A} and patented^{311A} baths for depositing both the metal and its alloys, but some of their claims for success in plating pure molybdenum were disputed.^{275B} Seim and Holt^{111A, 275A} plated alloys with iron, cobalt, and nickel from a citrate bath; McElwee and Holt^{200A} plated ternary alloys of cobalt, molybdenum, and tungsten. Ma^{188A} plated chromium alloys from a chromic acid molybdic acid bath; he also^{188B} deposited molybdenum oxide from a molybdate bath and then reduced it to the metal with hydrogen.

Molybdenum has been deposited from alcohol solutions³⁰⁴ and from liquid ammonia,⁴⁴ though the latter has been questioned.³³ In one of the bright zinc plating processes the deposit contains up to 1% molybdenum.²⁹⁹

NIOBIUM

The principal reports of the electrodeposition of niobium are by Izgarischev and his co-workers,^{148, 150, 260} who used solutions of Nb_2O_5 in KOH with additions of organic acids such as citric and oxalic. Temperature was 80°C, and c.d. 90–270 amp/sq ft. Niobium has some valuable properties which might make it attractive as a plating metal, but the published reports await independent verification.¹⁴⁴ Some Japanese patents^{171A, 171D} claim deposition of niobium from unspecified complex salts.

POLONIUM

The electrochemistry of this rare radioactive element has been reviewed by Haissinsky.¹¹⁶ It can be deposited by immersion on many metals, and can also be electrodeposited.⁵³ Considering its extreme scarcity, it is interesting to note that a commercial use was found for

polonium: it was claimed to improve the performance of spark plug electrodes.^{68, 70, 238B}. Most of the investigations of this element are of theoretical interest only (Refs. 52B, 115, 118A, 127, 144, 154, 155, 201, 242, 263).

PROTACTINIUM

The electrochemical behavior of this rare radioactive element has been reviewed by Haissinsky,^{117, 314} Bouissieres,³⁷ and Danon and Ferradini.^{62A}

RARE EARTHS

Except for lanthanum and cerium (q.v.) little has been published on the electrochemistry of the rare earths. Broughall⁴¹ claimed the deposition of some (unspecified) rare-earth metals from solutions of the halides, nitrates, cyanides, or thiocyanates in liquid ammonia. Fractional electrolysis has been used to separate the rare-earth metals.^{64, 65, 66, 145, 208}

RHENIUM

Rhenium is commercially available in limited quantities. According to Fink and Deren⁸² good deposits of it can be obtained relatively easily from various baths, including phosphates, oxalates, and alkaline solutions, but sulfate baths are preferred. One formulation is: KReO₄, 11 g/l; conc. H₂SO₄, 3.3 g/l; pH, 0.9; temperature, 25° to 45°C; c.d., 90 to 130 amp/sq ft. Perrhenic acid may be substituted for the potassium perrhenate.

The same authors report that the hardness of rhenium is 250 Brinell as plated, when chromium is 400.* It is mirror bright if plated on a polished surface, has high resistance to HCl, and may be codeposited with nickel and cobalt. Young³¹² suggested increasing the acid concentration in Fink and Deren's solution. The corrosion resistance of the deposit has been questioned.¹⁸⁸ There are several additional mentions of rhenium plating^{5, 128, 144, 215, 235, 289, 293} but few after 1938, about which time interest in the subject appears to have died out, until it was revived by Netherton and Holt,²³⁰ who reviewed the literature, confirmed the fact that sulfate baths were preferred, and offered a citric acid bath as an alternative. They also reported the deposition of alloys of rhenium with iron, cobalt, and nickel.^{230A} A patent to Levi^{248A} suggests heating the deposit to change its crystalline form. Druce^{69A} has published a monograph on rhenium.

* The hardness of chromium plate is closer to 900 Brinell.

SELENIUM

Selenium may be deposited from selenious acid solution.⁷⁰ Several authors have reported that continuous deposition is possible only if another metal is codeposited,^{187, 212} and it is at least true that the principal uses of selenium have been as minor additions to other baths as brighteners. The addition of SeO_2 to nickel baths has been suggested,^{121, 226} and silver selenide is claimed to brighten cyanide silver plate.²⁰⁸ Recently Bloom and von Hippel^{28, 208A} have patented a process for depositing selenium on the anode, from selenide solutions, for rectifier applications. Kofron^{170A} has patented a solution of sodium selenite plus HCl for a similar application; and Modjeska and co-workers^{222A} have advocated the use of essentially water-free solutions in phosphoric acid.

TANTALUM

There are several reports of tantalum deposition in the literature, but the evidence is not convincing. Izgarishev and Prede¹⁵¹ claimed to deposit tantalum from solutions containing glucose, potassium salicylate, and resorcinol; but Holt¹⁸⁴ was unable to repeat. Strongly alkaline solutions are recommended in a German patent;²⁵⁸ and Armstrong and Mcnefee, in a series of patents which appear to include a large portion of the periodic table,¹⁰ have used fluoride solutions, either acid or alkaline. Alloys of tantalum with iron or cobalt are also claimed by these workers. Mey²²⁰ uses tantalum or chromium to obtain a spangled effect when deposited on a shiny base metal. Broughall⁴¹ claims to have deposited tantalum from liquid ammonia solutions. A series of Japanese patents claim deposition from "complex salts,"^{171A, 171D} and unsupported statements that tantalum has been electroplated have appeared.^{183A}

Other references are given by Hopkins,¹⁴⁴ who concludes that, in spite of the many attempts to deposit tantalum from aqueous solution, the results are not encouraging; Seim and Holt²⁷⁵ have announced the same conclusion.

TELLURIUM

Though tellurium can apparently be deposited rather easily from aqueous solution, it is doubtful whether the deposit would have any practical value. Lenher¹⁸⁰ said that the properties of the metal suggest its use in electroplating, but Mathers and Turner²⁰⁰ did not agree, stating that its extreme brittleness would bar its use. The latter

authors found that a solution containing TeO_2 300, HF (48%) 500, and H_2SO_4 200 g/l, at c.d. 15 amp/sq ft and room temperature, gave good deposits at high efficiency and with no need for addition agents. Lukas and Jilek¹⁸⁵ used an ammonium sulfate-tartrate solution containing malonic acid and a small amount of a tellurium compound; Müller²²⁷ merely dissolved TeO_2 in sulfuric acid. Tellurium, like selenium, has been used as a brightener in nickel baths.^{46, 124}

THALLIUM

Brown and McGlynn¹⁶ obtained good deposits of thallium from a perchlorate bath containing peptone and cresylic acid, at c.d.'s around 9 amp/sq ft; the bath contained 40 to 120 g/l TiClO_4 and 60 g/l free HClO_4 . Sulfate and fluosilicate baths were not satisfactory. Kohlschutter and Good¹⁷¹ made a theoretical study of the Ti_2SO_4 bath; Parks and LeBaron²¹³ studied the deposition of thallium alloys. The older literature is reviewed by Mellor.²⁰⁷ Piontelli²⁵¹ obtained good immersion deposits on a rotating zinc rod from a solution of TlSO_3NH_2 (sulfamate) 120, $\text{Ba}(\text{SO}_3\text{NH}_2)_2$ 230 g/l. If the rod was not rotated, the deposit was spongy and non-adherent.⁸¹ Bertorelle and co-workers^{20A} have studied the deposition of thallium and its alloys from fluoroborate baths.

Yntema and Audrieth³¹⁰ deposited thallium from solutions of TlI and TINO_3 in liquid ammonia; and from solutions of Tl salts in acetamide and formamide.³¹¹ Booth and Merlub-Sobel³³ also investigated liquid ammonia solutions, and Plotnikov and Gorenbein²⁵⁵ obtained deposits of thallium from an organic bath using ethyl bromide as solvent.

THORIUM

Fink,⁷⁰ and Fink and Jones⁸⁶ claimed thorium deposition from an alkaline solution of ThO_2 and a trace of a salt of another metal to act as a "depolarizer." The recommended bath contains 52 g/l Na_2CO_3 , 21 g/l ThO_2 , 60 g/l dextrose, and a trace of $\text{Ni}(\text{OH})_2$ or a zinc salt. Temperature is 80°C. Marden and co-workers¹⁹⁰ patented a solution of $\text{Th}(\text{OH})_4$ in HBF_4 or H_2SiF_6 ; or ThCl_4 and potassium lactate: in this case also the presence of another metal is desirable, lead and iron being recommended. The deposit is a thorium alloy. Booth and Merlub-Sobel³³ could obtain no deposit of thorium from anhydrous ammonia solutions; Atanasiu and Babor¹³ obtained non-metallic deposits of a thorium compound from ethyl alcohol solutions; but Cotelle and Haissinsky⁶⁰ reported that thorium could be deposited on a silver

cathode from solutions of thorium nitrate in ethyl alcohol in the presence of 15 to 20% acetone and a trace of water. Its deposition from a "complex salt of an organic acid" has been claimed.^{171B, 171D} See also Ref. 51A.

TITANIUM

Efforts to electrodeposit titanium have led to ambiguous results. More than a hundred years ago Becquerel^{18, 200} electrolyzed a concentrated HCl solution of titanium and iron chlorides with platinum electrodes and obtained a deposit which was said to contain titanium, though if the iron was omitted there was no deposit. deBussy⁵⁰ reported a silver-white plating of titanium from a solution of potassium titanate, sodium sulfate, and sulfuric acid. A solution of titanium sulfate in anhydrous sulfuric acid is reported²²⁵ to yield the metal; other solutions which have been recommended are Ti(OH)_4 in sulfanilic acid;¹¹² $\text{Ti}(\text{SO}_4)_2$ in aqueous sulfuric acid containing sodium sulfate;¹¹⁸ strongly alkaline titanate solutions.²⁵⁷ Fink and Jones, in the patents already referred to,^{79, 86} claimed deposition of titanium from: 10 g/l TiO_2 , 15 cc/l HF (or 30 cc/l 50% HF), 10 cc/l HCl, 0.5 g/l gelatin; 80°C and about 150 amp/sq ft. Traces of copper are recommended as a "depolarizer." Keyes and Swann¹⁶² could not plate titanium from aqueous solutions.

TUNGSTEN

Perhaps more effort has been expended on attempts to develop a practical process for plating tungsten than on any of the other elements under consideration here—perhaps indeed more than all the rest combined. Tungsten electroplates would undoubtedly have utility, and, although the metal is relatively expensive it is not so much so as to bar its use in specialized applications. The success of chromium plating has no doubt spurred efforts in tungsten deposition, for the chemistry of the two metals is at least formally similar. Despite this quantity of effort, however, it remains doubtful if pure tungsten has been deposited from aqueous solution; tungsten alloys can be plated, but until very recently they have shown little promise of commercial utility.

The literature of tungsten plating goes back to 1809.²¹⁸ Most of the earlier workers reported that solutions of tungstates or salts of hexavalent tungsten were reduced at the cathode to compounds containing the metal in a lower state of oxidation, and not to the metallic form. Fink and Jones, whose patents have already been repeatedly

cited,^{70, 86, 87} were among the first to claim successful tungsten deposition, though their results have been questioned. These authors used highly alkaline hot solutions of tungstates: a typical bath contained Na_2CO_3 330, WO_3 125 g/l, at 100°C, c.d. 200 amp/sq ft, and platinum anodes. The presence of a trace of "depolarizing metal" was very beneficial or even necessary; this fact prompted Holt¹³³ to observe that the deposits were not pure but always contained the trace metal, and a short polemic ensued.^{80, 136, 156} Earlier Holt and Kahlenberg¹³⁹ had reported that tungsten could be plated from: Na_3PO_4 100 g, WO_3 30 g, and water 150 cc, temperature 90° to 100°C, c.d. 90 amp/sq ft. The cathode efficiency was less than 1%, and the bath became inoperative after a while and could not be reconditioned. The early exhaustion of the bath suggests the deposition of some impurity unsuspected at the time, and checks well with Holt's later views.

Gol'ts and Kharlamov¹⁰⁶ made observations in agreement with Holt's reports. Other Russian workers²⁸⁰ recommended periodic additions of NiSO_4 , under which conditions thick deposits (0.2 mm) were obtained. Glazunov and Jolkin^{103, 104} investigated similar baths; Glazunov¹⁰² claimed that, at 90°C, pure tungsten can be deposited, though only as a thin layer. Other workers have noted that traces of iron are necessary for plating to proceed.

Between 1935 and 1939 a formidable series of patents were issued to Armstrong and Menefee^{10, 11} which dealt with the electrodeposition of tungsten from fluoride baths, and according to Dubpurnell⁷⁰ this process did have some limited commercial use. A typical formulation is given as:¹¹ a reaction product of WO_3 or a derivative thereof, with an alkaline bifluoride; the bath may contain other halides as well as H_3BO_3 and tartaric acid. Tungsten alloys may also be plated, as by the addition of NiCO_3 . The anodes may be platinum, tungsten carbide, or a mixture of tungsten carbide and the alloying metal.

Space does not permit detailed review of all the other references cited in the bibliography (Refs. 56, 91, 144, 158, 158A, 162, 170, 173, 182, 213, 231, 247, 258, 289, 308). The most recent claim to pure tungsten plating appears to be that of Harford,¹²³ which involves an aqueous solution of an alkyl hydrocarbon polyamine (e.g., diethylene triamine).

Broughall,⁴⁴ in a rather all-inclusive patent, lists tungsten among the metals platable from liquid ammonia solutions; but Booth and Merlub-Sobel⁸⁸ were unable to plate the metal from this solvent. The Wolfram Lampen AG, in two German patents,³⁰⁵ describe methods for plating tungsten from acetone solutions of the hexachloride, or per-tungstic acid in water, alcohol, or ether; but, again, attempts to repeat by others were fruitless.^{87, 92}

The situation with regard to the deposition of tungsten alloys is much more clear-cut. Tungsten has been codeposited with nickel,²⁰ copper,¹⁰⁷ platinum,¹⁵⁰ iron,¹⁶ and chromium.^{266A} Holt and his co-workers have published many reports on the deposition of tungsten alloyed with iron, nickel and cobalt (Refs. 52, 131, 133, 135-138, 140-142, 183, 234). In recent papers Holt and Vaaler¹¹³ and Clark and Lietzke^{52A} have offered a mechanism for the deposition process, attempting to explain the function of the alloying metal in allowing deposition to proceed.

Brenner and co-workers¹² have recently developed a process for plating cobalt-tungsten alloys which appears to have promise of commercial usefulness. These deposits are characterized by their high hardness, especially hot, and are superior to chromium in throwing power and efficiency. Similar solutions have been described in Germany^{238A} and India.^{277A} Pollack^{258A} has reviewed the status of tungsten plating in Germany.

URANIUM

Most reported attempts to deposit uranium have yielded negative results. Mellor²¹¹ summarizes the early work; Hopkins¹⁴¹ concluded that even non-aqueous solutions failed to produce results. A Wolfram Lampen AG patent,³⁰⁵ noted under tungsten, claims uranium deposition also, from acetone solutions. Eastman^{70A} electrolyzed UBr₄ or UBr₃ in solvents such as ethanol, formamide, acetamide, or glacial acetic acid. Heal¹²⁵ has reviewed the electrochemistry of the element.

VANADIUM

Two independent observers reported that they had succeeded in plating vanadium by an identical process, but later work has tended to refute their claims. Cowper-Coles^{60, 211} said he obtained brilliant metallic deposits of vanadium from 1.75 parts V₂O₅, 2 parts NaOH, 160 parts water, 32 parts HCl, c.d. 18 to 20 amp/sq ft, 1.88 v, carbon anode and platinum cathode. Gin¹⁰¹ confirmed and improved the solution by adding fluoride ion. Nevertheless Fischer⁹³ made a thorough study of the process and was unable to repeat the deposition; he also gave a complete literature review, to which reference may be made for further citations. Very little has been added to the literature on vanadium deposition since Fischer's paper (published in 1916). Keyes and Swann¹⁶² reported failure to obtain a deposit, and a German

patent reports that the metal can be plated from strongly alkaline solutions saturated with vanadium oxide.²⁵⁸

WOLFRAM

See Tungsten.

ZIRCONIUM

Becquerel in 1831¹⁷ electrolyzed a solution of $ZrCl_4$ and a small amount of $FeCl_3$ in a divided cell and said he obtained a deposit of zirconium. Fink and Jones⁸⁶ recommended excess $Zr(OH)_4$ suspended in 10% Na_2CO_3 plus a small quantity (?) of sulfuric acid to bring the pH to 5.0 to 5.2, at 80°C. Bradt and Linford⁸⁸ reviewed the literature and investigated possible processes. They may have succeeded in depositing extremely thin layers of zirconium from solutions of sodium and zirconyl sulfates, under carefully controlled conditions. A recent patent²⁸¹ assumes the possibility of zirconium plating from "aqueous complex sulfate baths." Kita and associates,¹⁶⁶ however, dispute this claim and conclude that there is hardly any possibility of obtaining zirconium from aqueous solution. Koizumi and co-workers^{171C, 171D} claimed to deposit the metal from complex salts; but, again, Holt^{136A} failed to obtain deposits by any of the published methods of which he offers a bibliography.

A recent patent describes the deposition of zirconium from a non-aqueous solution of the oxychloride in butanol.^{221A} Electrophoretic deposition from alcohol solutions has been patented.^{281B} It is claimed that zirconium can be plated on a cathode with which it will alloy from aqueous solutions containing a reducing agent.^{156A}